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# A NEW THEORY OF COHESION APPLIED TO THE THERMODYNAMICS OF LIQUIDS AND SOLIDS.

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§ 1. The phenomena of surface tension, elasticity and latent heat prove that between the particles of matter, whatever they may be, there is an attraction which must be some function of the distance between them. It is this attraction against which work is done by expansion; and since work is the product of force and distance, we may obtain a measure of cohesion when we know the coefficient of expansion and the difference of the specific heats of a body under constant pressure and under constant volume.

The latter, unfortunately, in the case of solids and liquids, has not been accurately determined, so that this simple measure cannot be applied; but since the specific heat of liquids invariably exceeds that of their vapors at the same temperature, and the liquid coefficient of expansion is less, the cohesion in the liquid state must be much greater than in the state of vapor; and we may roughly calculate, in certain cases, the law of its variation.

We have, for instance, for boiling water, a specific heat of 42,000,000 ergs (C. G. S.), while that of steam, under constant volume, is 15,600,000 ergs, nearly; the difference being 26,400,000, and the coefficient of voluminal expansion of water at 100° being (apparently) .0007, a force of 38,000,000,000 dynes (C. G. S.) must be overcome in order to account for this work. The pressure of saturated steam is less than its calculated value,

according to Gay-Lussac, by from 600\* to 5000 dynes.† The expansion into vapor being nearly equal to 1630 volumes of the boiling liquid shows that the cohesive attraction must have diminished between seven million and seventy million times, while the distance from particle to particle must have increased in the ratio of the cube root of 1630, or 11.75. In this case, therefore, we might infer that the cohesive attraction per unit of surface varied inversely as some power of the molecular distance not less than six and not greater than seven and one-half, a mean value being the most probable; and remembering that the number of particles which exert this attraction diminishes as the square of the distance increases, the molecular attraction would vary according to the fourth or fifth power, inversely.

For alcohol, in the same way, the coefficient of expansion at 78° being .0013, the total expansion into vapor about 455 volumes, and the difference of specific heats, 15,000,000 ergs, the cohesion is about 12,000,000,000 dynes per square centimetre, and since the pressure of the saturated vapor according to Gay-Lussac,‡ reduced by suitable formulae, is 15,000 dynes less than the theoretical value, it would appear that the molecular attraction varied as the four-and-two-thirds power, inversely.

For ether we find a difference of specific heats of only 4,000,000 ergs, and a coefficient of expansion .0017, indicating about 2,400,000,000 dynes for the cohesion; the expansion into vapor is about 235 volumes, and the pressure of cohesion of the vapor, deduced from Gay-Lussac's figures,§ is 14,000 dynes, also indicating the four-and-two-thirds power of the distance.

These are the only liquids which I can find, the density

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\* Allowing for the space occupied by the molecules. See Zeuner, Chap. I, III, *Chaleurs latentes interne et externe*.

† See Deschanel's *Natural Philosophy*, Part II. §283-284.

‡ See Zeuner, French Translation, 1869, page 282.

§ Zeuner, *ibid*.

of whose *saturated* vapors has been satisfactorily determined; and the indication is clearly that the cohesive attraction varies inversely as some power of the distance between four and five.

The constancy of this law may be established by comparing the tables for latent heats and surface tensions. The latter is easily seen, as Sir William Thomson and others have pointed out, to represent, numerically, a large fraction of the work necessary to volatilize a film of the thickness of one molecule; and neglecting this thickness, which does not vary through wide limits, we shall find that the surface tension and latent heat are approximately proportional. That is, not only the equivalent of the work necessary to separate a liquid into the thinnest possible laminae (or films) is approximately proportional to that necessary to volatilize it completely, but also both of these quantities are determined by the attraction of the molecules for each other, which could not be the case unless the law of variation of this attraction were the same, or nearly the same, for all liquids.

In no matter what way the cohesive pressure is calculated, we find that the latent heat varies very nearly in proportion; thus the total latent heat of steam is 536 units, of alcohol vapor 202 units, and of ether vapor 91 units, corresponding to the order of the cohesive pressures already calculated, and also to the order of their surface tensions, 81, 26 and 19 (dynes per centimetre).

These points will be more carefully considered after an analytical investigation of the actual relations which must subsist and those which probably subsist between these various quantities; at present all the evidence of the facts is to show that the cohesive attraction between two molecules varies as the fourth or fifth power of their distance, inversely, and not as any power materially greater or less.

There are various points of view which would make it seem improbable that any such general truth can be estab-

lished, and this accounts, undoubtedly, for the fact that the laws of cohesion have hitherto escaped a systematic investigation. These considerations will be met later on. It would seem, moreover, at first sight, that a multitude of solutions might be possible, each equally capable of explaining the various phenomena by means of a sufficient number of arbitrary assumptions—a number continually increasing, as new facts are discovered, until, like the corpuscular theory of light, the whole structure would fall as if by its own weight, under the blows of some simpler hypothesis.

Such is not the nature of the present investigation, which adds nothing to the assumptions already required by the molecular theory save one, which is shown to be the necessary consequence of various phenomena.

The object of this paper will be to investigate more fully the nature of the law of cohesion and to apply it to the solution of the relations existing between certain physical constants well known in thermodynamics. It may be stated that these have been generally viewed, hitherto, from a purely empirical standpoint.

§ 2. There are evidently three distinct pressures which exist in a liquid or solid: first, the external pressure ( $P$ ); second, the kinetic pressure ( $P'$ ), due to the vibration of the molecules; and third, the cohesive pressure ( $P''$ ), due to the attraction of these molecules for each other. If these pressures are all expressed in the same unit (dynes per square centimetre), and are reckoned positively outwards, we have for a body in equilibrium the expression,

$$\bar{P} + P' + \bar{P}'' = 0,$$

the line drawn over  $P$  and  $P''$  indicating that their true direction is inwards.

The rough investigation of § 1 is probably sufficient to show that in vapors,  $P''$  in liquids and solids,  $P$  may generally be neglected; so that in vapors  $P$  and  $P'$ , in liquids and solids,  $P''$  and  $P'$  are very nearly equal and opposite. That is, in liquids and solids, the cohesive pressure plays the same part as does the external pressure in vapors.

The well-known formula connecting the volume,  $V$ , the pressure,  $P$ , and absolute temperature,  $T$ , of a gas,

$$\frac{PV}{T} = \text{constant},$$

or, in the form used largely in the kinetic theory,

$$PV = \frac{1}{3} Mv^2,$$

where  $M$  is the mass and  $v^2$  the mean square of the molecular velocity, is established upon the assumption that the molecules of a gas are small as compared with the distance between them. If the molecule has any size, that is, if it prevents other molecules from approaching within certain definite limits, the free path ( $l$ ) will in all cases be shortened by an amount ( $l'$ ) which I propose to call the molecular diameter. The present investigation proceeds on the usual hypothesis that the latter is nearly, at least, constant.

Since then the free path is shortened in the ratio of  $l$  to  $l-l'$ , the kinetic pressure will increase, *cæteris paribus*, in the same ratio, and we shall have for solids and liquids,

$$P'V = \frac{1}{3} Mv^2 \frac{l}{l-l'}.$$

The kinetic theory asserts that two bodies are at the same temperature when their molecular kinetic energies are equal, that is, when

$$\frac{mv^2}{2} = \frac{m_1v_1^2}{2},$$

and that furthermore

$$\frac{T}{T_0} = \frac{\frac{mv^2}{2}}{\frac{mv_0^2}{2}}$$

whence combining, and denoting by  $m$ , the mass of a hydrogen molecule, and by  $v_0^2$  the mean square of its velocity at the freezing temperature of water ( $T_0 = 273^\circ$ ), we have, remembering that the density  $D$  is the quotient of  $M$  and  $V$ ,

$$P' = \frac{1}{3} Dv_0^2 \frac{m_1}{m} \frac{T}{T_0} \frac{l}{l-l'}, \quad \text{I.}$$

the fundamental formula in the kinetic theory of liquids and solids. If we suppose  $l'$  very small as compared with  $l$ , this formula immediately reverts to one of the forms well known in the theory of gases.

Let us now suppose that a body on being heated  $1^\circ$  expands freely by the small ratio  $\epsilon$ ; and that it is again compressed at constant temperature to its original volume. Designating by  $E$  the modulus of voluminal elasticity (after Maxwell), or *coefficient of resilience* (after Everett) under constant temperature, we shall require by definition an external pressure,  $E\epsilon$ , equal and opposite to the increase of internal pressure due to heat. The volume being unchanged, the density must be the same; and if there be no change in the molecular arrangement, the factor  $l + (l-l')$  must be unchanged; so that the only variable in equation I. is  $T$ , which has increased from a value,  $T$ , to the value  $T + 1^\circ$ , thus causing an increase of the kinetic pressure equal to

$$\frac{1}{3} Dv_0^2 \frac{m_1}{m} \frac{1}{T_0} \frac{l}{l-l'} = \frac{P}{T} = E\epsilon,$$

from which we see that

$$E\epsilon T = P' = \frac{1}{3} Dv_0^2 \frac{m_1}{m} \frac{T}{T_0} \frac{l}{l-l'}, \quad \text{II.}$$

that is, the continued product of the coefficients of voluminal elasticity and expansion with the absolute temperature is equal to the kinetic pressure.

This theorem applies only to liquids or solids in which no molecular rearrangement is brought about by heat or pressure, and which consequently agree, like gases, in obeying the same general laws of expansion. An examination of the tables will show that most liquids fall under this category. The most important exception is water, which we shall see, from many considerations, is not to be treated as a pure liquid, even at moderately high temperatures. In such liquids,  $l'$  may be treated as a variable, and there is no connection between the real and apparent compressibility and expansion.

The theorem is, in other respects, perfectly general, and gives, for gases (in which  $\epsilon T = 1$  by the Law of Charles),  $P' = E$ , as it should be. The importance of the theorem, in determining readily the free path of a molecule and the measure of cohesion for liquids and solids, has apparently been overlooked. The application to liquids is restricted only by the paucity of those whose elasticity has been determined, and its extension only by our ignorance of the real nature of the law which governs molecular cohesion.

Let us therefore assume that the force between any two molecules in the line joining them varies as the  $\alpha$ th power of their distance, inversely; then the component of this attraction in any direction will also vary as the  $\alpha$ th power inversely; and if we conceive of a perfectly homogeneous and uniform expansion in which every line is increased in a certain ratio, called the ratio of linear expansion, so that the angles subtended by a particle are in no case altered, nor the direction of any line fixed in it, then the component of the attraction of every particle for every other, resolved in any one direction, will also vary as the  $\alpha$ th power of the linear expansion, inversely, no matter how the



particles may be situated with respect to the common line of resolution; and hence the resultant force of cohesion, perpendicular to any surface, due to the action of all particles on one side of that surface upon all particles on the other, will also vary as the  $x$ th power, inversely, of the ratio of expansion, while the area of the surface separating a given number of molecules will vary inversely as the square of the ratio of expansion. It follows that the resultant cohesion  $P''$ , measured in dynes per square centimetre of surface, will vary inversely as the  $x + 2$  power of the ratio of linear expansion.

Denoting, therefore, by  $P''_0$  the value of the cohesive pressure when the volume is  $V_0$  and the average molecular distance  $l$ , we shall have

$$\frac{P''}{P''_0} = \frac{l_0^{x+2}}{l^{x+2}} = \frac{V_0^{\frac{x+2}{3}}}{V^{\frac{x+2}{3}}}$$

also, taking logarithms,

$$3 \log l - 3 \log l_0 = \log V - \log V_0$$

whence, by differentiation,

$$3 \frac{dl}{l} = \frac{dV}{V}.$$

Now it is established in thermodynamics that the work  $\delta W$  done in the (small) expansion  $\delta V$  against the pressure  $P''$  is

$$\delta W = P'' \delta V,$$

hence the total work necessary to overcome the cohesive forces in expanding from a volume  $V_1$  to a volume  $V_2$  will be

$$\Delta W = \int_{V_1}^{V_2} P' dV = P''_0 \int_{V_1}^{V_2} \left( \frac{V_0}{V} \right)^{\frac{x+2}{3}} dV.$$

If between the limits,  $V_1$  and  $V_2$ ,  $\alpha$  can be regarded as constant and equal to  $\alpha$ , we have

$$\Delta W = \frac{3}{\alpha - 1} P_0'' V_0^{\frac{\alpha+2}{3}} \left( \frac{1}{V_1^{\frac{\alpha-1}{3}}} - \frac{1}{V_2^{\frac{\alpha-1}{3}}} \right)$$

whence if  $V_0 = 1$  we may write

$$\Delta W = \frac{3}{\alpha - 1} P_0'' \Delta V^{\frac{1-\alpha}{3}}$$

hence we have, for the total work required for completely vaporizing the unit of volume of a body, at constant temperature,

$$W = \Sigma \Delta W = \Sigma_{V=1}^{V=\infty} - \frac{3}{\alpha - 1} P_0'' \Delta V^{\frac{1-\alpha}{3}}.$$

It is easily seen that if  $\alpha_2$  be the maximum value of  $\alpha$ , during expansion, and  $\alpha_1$  the minimum value, greater than 1,

$$W > \frac{3}{\alpha_2 - 1} P_0''$$

$$< \frac{3}{\alpha_1 - 1} P_0''$$

for, since  $V$  is necessarily greater than 1, each term in the series is greater than  $\frac{3}{\alpha_2 - 1} P_0'' \Delta V^{\frac{1-\alpha_2}{3}}$  and less than

$$\frac{3}{\alpha_1 - 1} P_0'' \Delta V^{\frac{1-\alpha_1}{3}}.$$

It follows that, independent of any theory of cohesion, if the force be known to vary inversely as some power of the molecular distance not greater in any case than  $\alpha_2$  and not less than  $\alpha_1$ , the internal latent heat of vaporization of the unit of volume of any substance is known within two limits, in terms of the cohesive pressure  $P_0''$ , under which the substance exists in the original state.

Thus we have a mathematical proof of the statement in § 1, concerning the mutual dependence of latent heat and cohesion.

The possibility of such a connection, independent of the choice of units, is easily established by the consideration that the dimensions of work per unit of volume and pressure per unit of surface are the same, a consideration by which the discovery of some law like that alluded to might have been anticipated.

Denoting by  $a$  some value of the variable  $\alpha$  between  $\alpha_1$  and  $\alpha_2$ , a value which, although perfectly definite in any case, is known only to lie within these limits, we have for the internal latent heat,\*  $L$ , of the unit of volume, whose mass is  $D$ , the equation,

$$JLD = \frac{3}{a-1} P_0'', \quad \text{III.}$$

where  $J$  is the mechanical equivalent of heat, and remembering that  $-\bar{P}_0'' = \bar{P} + P'$  we have, numerically,

$$JLD = \frac{3}{a-1} (\bar{P} + P'),$$

where  $\bar{P}$  may generally be neglected.

Combining with II. we have

$$JLD = \frac{3}{a-1} (\bar{P} + E\epsilon T), \quad \text{IV.}$$

an equation by which the value of  $a$  can be determined.

For a given value of  $a$  there will be an indefinite number of possible theories by which this value can be realized, but of this number one only is likely to be plausible. On the other hand, given any theory of the cohesive force, the value of  $a$  will be absolutely determined in every case, so that we shall be able at once to decide for or against the theory.

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\* The *internal* latent heat (which will be understood throughout this paper) is that necessary to convert the unit of weight of a substance into vapor of the same temperature without doing external work.

§ 3. The necessary data appear to have been determined only for the five liquids in the table: — \*

	<i>L</i>	<i>D</i>	<i>E</i>	$\epsilon$
Water	575.43	1.000	20.2 { thousand million	— .00005
Alcohol	223.43	0.806 +	12.15 “	+ .00105
Ether	86.48	0.736	8.8? “	+ .00150
Carbonic bisulphide	82.79	1.27	16.0 “	+ .00114
Turpentine	66. ?	0.89	13.7 “	+ .00071

$$\mathcal{F} = 42,000,000. \quad T = T_0 = 273^\circ$$

The case of water must be thrown out for reasons already mentioned, which will be treated in full, later on.

We find for alcohol,  $\alpha = 2.38$ ; for turpentine,  $\alpha = 4.23$ ; for bisulphide of carbon,  $\alpha = 4.31$ , and for ether  $\alpha = 5.04$ . With the exception of alcohol, the numbers agree closely enough with those obtained from the rough calculation of § 1, although the latter were derived from the ratio of the cohesive forces in two widely different states of aggregation, while the values of  $\alpha$  were determined by the work done against a cohesion continually decreasing during the change of state.

We are not able from these data to determine exactly what the law of cohesion is; but we are able to decide what it is not. Since  $\alpha$  is a value intermediate between two values of  $\alpha$ , namely  $\alpha_1$  and  $\alpha_2$ , some values of  $\alpha$  must be equal to or greater than  $\alpha$ , and some values equal or less.

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\* With the exception of turpentine, the (internal) latent heats were from Zeuner's Tables (appendix); the densities from Wöhler's Organic Chemistry (indexed); the elasticity was the mean from Everett, pages 52 and 53 of his Units and Physical Constants; and the expansion is the mean of Kopp and Pierre. For turpentine, see Everett, page 88; Pickering's Physical Manipulation, Volume II., Appendix, Table 12; Ganot's Physics, § 334 and § 326.

Hence no force can explain the laws of cohesion which is not capable of varying, inversely, as a power of the distance which is greater in some cases than four at least, and less in others than  $2\frac{1}{3}$ . It would therefore appear that the law of universal gravitation, which requires a variation at great distances according to the inverse square, cannot explain the phenomena of cohesion; neither can any force which disappears completely in the state of vapor.

We have seen the conditions required by the considerations of the preceding sections. The only forces known to physics which can by any possibility satisfy them are those involving both attraction and repulsion, that is, polarity in some form.\*

There is, however, a possibility of error in the result of any reasoning, no matter how many facts may have been gathered to support it; and in most minds there will be found an unwillingness to limit in any way the application of such a general truth as the law of universal gravitation, the beauty of which, if it could be adapted to the explanation of the laws of cohesion, would be admitted by all. It is to answer this objection, and to prove, once for all, that the law of universal gravitation can never explain the phenomena in question, that the following proof is added of a proposition which might be considered self-evident.

Let us suppose that the attraction between different particles varies inversely as the  $x$ th power of the distance; then the potential will vary inversely as the  $x - 1$ <sup>st</sup>. The potential at the common centre of a series of nearly spheri-

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\* It is true that, in one sense, the law governing all forces, properly so called, is fundamentally the same, being reducible to elements attracting or repelling inversely as the square of the distance; nevertheless, in effect, forces are essentially different.

Two small systems of electrified points, neither being charged as a whole, will in general attract each other inversely as the fourth power of the distance. Small circular currents or electric vortices will do the same; and this is also the law for small magnets under certain conditions. (See Maxwell, Volume II., § 388.) Arranged in different ways, two particles of magnetized matter may attract inversely as the square, the fourth power, or again inversely as the seventh power of the distance; and the probable resultant of an indefinite number of such particles will be found to vary inversely as some power between the fourth and fifth of the average distance between them.

cal shells whose mean radii are proportional to the numbers 1, 2, 3, 4, etc., into which all the particles of a body may be considered as distributed in numbers proportional nearly to the squares of the radii, will be a constant multiplied by the series,

$$1 + \left(\frac{1}{2}\right)^{x-3} + \left(\frac{1}{3}\right)^{x-3} + \left(\frac{1}{4}\right)^{x-3} + \text{etc.},$$

or its equivalent as far as convergence is concerned. Now it is well known that, unless the exponent in this series were greater than unity, the series would not converge; accordingly the potential at any point would depend upon the whole quantity of surrounding matter, and not merely upon the nature and distribution of the substance in the immediate neighborhood; hence the latent heat would be governed, not only by the amount vaporized, but also by that which remained in the liquid or solid state. That is, a definite latent heat for a given substance would be impossible unless  $x-3 > 1$ . We conclude that it is absolutely necessary that the attraction between different particles of a body, upon which latent heat depends, should vary, on the whole, inversely as some power of the distance greater than the fourth, so that this application of the law of universal gravitation must finally be abandoned.

A number of facts, based upon the variations of specific heat in the liquid state and the departures in gases from the Law of Boyle and Mariotte, might be brought forward to support the evidence already adduced; enough has probably been said to prove that if the phenomena are to be solved at all, it must be by some force which varies, for the most part, inversely as the fourth or fifth power of the distance.

§ 4. Having proved that a force of no other type can explain the phenomena arising from cohesion, it is now of

interest to inquire whether there are any known forces, similar to those of electric or magnetic action, which may be adequate to this task; and the following sections are accordingly devoted, for the most part, to the analytical investigation of the consequences of various suppositions.

The solution of problems in the theory of cohesion can only be obtained through some simple hypothesis; and the first which we shall examine is that the normal attraction of two particles is inversely as the fourth power of the distance. The investigation of the theory of cohesion from this point of view will be greatly facilitated by the study of the attraction and repulsion of small magnets, the laws for which are apparently identical with those which we have supposed.

Since any distribution of magnetism may be represented as the resultant of an indefinite number of very small magnetized particles, arbitrarily arranged, no matter what the shape of these particles may be,\* I shall assume for convenience, in this investigation, that the ultimate particles of matter which need be considered are analogous to small uniformly magnetized spheres, which may or may not correspond to the chemical atoms. The correspondence, if any exist, will appear in this and in the next section.

The strength of field at any point, due to a uniformly magnetized sphere, may be represented by that due to a small magnet of equal moment at its centre;† hence the action of one magnetized sphere on another may be represented by that of a small magnet at the centre of the first upon the whole mass of the second sphere; but the action of the second sphere upon this small magnet would by the same proposition be equal to that of a second small magnet at its own centre; and therefore, since action and reaction are equal and opposite, two uniformly magnetized

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\* See Cumming, *Theory of Electricity*, Prop. I., page 225, et seq.

† See Cumming, *Theory of Electricity*, Prop. IX., page 276.

spheres must attract or repel exactly as two small magnets of respectively equal moments would do, if placed at their centres.

Since the field due to a small magnet is shown to vary in any direction inversely as the cube of the distance,\* the attraction for a second small magnet, measured by the difference of the action upon the nearer and farther pole, will vary as the rate of change of a force, itself varying inversely as the cube of the distance, which rate of change is seen at once, by the principles of the calculus, to vary inversely as the fourth power of the distance.†

So long, therefore, as the atomic arrangement is not disturbed, whether a substance be elementary or compound, the attraction between any two atoms according to the analogy will vary, as we have supposed, inversely as the fourth power of the distance, and therefore, in the perfectly homogeneous expansion described in the last section, the value of  $\kappa$  will be constant and equal to 4, so that we shall have

$$JLD = -P''. \quad \text{I.}$$

If, however, the substance be not elementary, we must remember that, in the state of vapor, the spheres (or atoms), which we have supposed to be completely separated, must afterward be reunited in clusters, so that a part of the energy required to separate them completely will not be needed. An approximation to the relative amounts of energy required to volatilize an element and a compound, respectively, will be found by considering from how many atoms a given atom is separated in each case, and what attraction is exerted by each atom from which it is separated.

It is of course impossible to obtain an exact solution without knowing the atomic grouping, both in the solid

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\* Cumming, *ibid.*

† See Maxwell, § 388.



or liquid and in the gaseous state; but we know that it is impossible for a given atom to be surrounded by more than twelve at equal distances from it and from each other, and that, in order to have thirteen or more, some of the central distances must be increased. In any compact atomic arrangement, we shall therefore not commit a serious error by assuming that there are twelve atoms at unit-distance from a given atom, forty-eight at two units' distance, and in general  $12 n^2$  at  $n$  units' distance.

Not knowing how these atoms may be arranged, we must apply the theory of probabilities to determine the potential at any centre due to all the surrounding atoms; and we shall find that this potential, like the probable error of the mean of a number of terms, is proportional to the square root of that number;  $n^2$  atoms at  $n$  units' distance will therefore through interference have a probable effect only as great as  $n$  atoms combined; and since the potential must vary, *cæteris paribus*, inversely as the cube of the distance, the effect of  $12 n^2$  atoms at  $n$  units' distance, as in the case of an indefinite number of magnetized particles, will be equal to that at unit-distance of  $12$  atoms divided by  $n^2$ . The whole number of atoms surrounding a given atom will therefore be equivalent, very nearly, to

$$12\left(1 + \frac{1}{2^2} + \frac{1}{3^2} + \frac{1}{4^2} + \text{etc.}\right)$$

atoms at unit-distance.

This series may be broken up into two, namely,

$$1 + \frac{1}{3^2} + \frac{1}{5^2} + \frac{1}{7^2} + \text{etc.},$$

which is shown\* to be equal to  $\frac{\pi^2}{8}$ , and a second series,

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\* Riemann's "Partielle Differentialgleichungen," § 23, fin.

$$\frac{1}{2^2} + \frac{1}{4^2} + \frac{1}{6^2} + \frac{1}{8^2} + \text{etc.},$$

which is easily seen to be one-fourth of the original series. Since, then, three-fourths of the series is equal to  $\frac{\pi^2}{8}$ , the whole series is equal to  $\frac{\pi^2}{6}$ .

We see, therefore, that the theory which we are investigating is not open to the criticism which caused us to abandon the theory of gravitation, since the potential, which determines the latent heat, is practically independent of the whole mass of a substance, provided only that it contain several layers of molecules or atoms, as we always suppose it to do.

The latent heat is the same as if about  $2 \pi^2$  atoms could surround a given atom, and for convenience in rough calculation we may call this number twenty.

It follows that a substance having two atoms in the molecule will require about one-twentieth less heat to volatilize it than if it had only one, since in the latter case each atom is practically separated from twenty others (whose interference may be neglected), while, in the former, one of these remains by its side. In the same way, if the molecule contain three or four atoms, clustered, the substance will require two- or three-twentieths less heat respectively; but when there are more than two atoms in the molecule, we may have a variety of atomic groupings possible, and to obtain even a rough measure of the latent heat, a knowledge of the graphical symbol will be necessary.

If the atoms be of different kinds, the solution becomes still more complex, and indeed impossible in the present state of our knowledge of the molecular constitution.\*

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\* See, however, Rühlmann, *Mechanischen Wärmetheorie*, Volume II., page 226 et seq.

A special device must be invented for approximation in each particular case; and although a solution of this sort is of course worthless for purposes of demonstration, it will be sufficient to show whether the facts are satisfied or not by the theory within reasonable limits, and if the error, introduced by the complexity of a molecule in a given case, is found to be small as compared to the whole quantity, we may suppose that any small mistake in the elimination of this error will have still less influence in the result.

We have reason to expect, *à priori*, that in any simple liquid the latent heat will be less than its uncorrected value by not more than fifty per cent.; and if we allow for a mistake of even twenty per cent. in calculating the correction, we ought not to be in error by more than ten per cent. in the result.

When the latent heat has been determined, we ought to be able to supply either the elasticity or the coefficient of expansion, with the same degree of approximation, wherever formula II. of § 2 applies. If a liquid be not simple, but compounded (chemically) of two, differing widely in their properties, especially if the union be not very intimate, we may shorten the calculation by treating the compound liquid as a mechanical mixture of its components. Thus ethyl hydrate (alcohol) may be treated as a mixture of 18 parts water and 74 parts ethyl oxide (ether), whereas the latter (ethyl oxide) would not be treated as a mixture of ethylene and water, even if we possessed the necessary data.

§ 5. In applying the rules and formulae of the preceding sections, it must be remembered that they were established on the assumption, which has not so far been questioned, that the ultimate atoms are perfectly elastic,

but nevertheless sufficiently hard to resist any change of shape induced by the sudden pressure of impact. In the case of gases and vapors, it is known that this yielding may be disregarded; but in liquids and solids we have no right to assume that the laws founded upon this assumption will be rigorously true. It must not be attempted, without a special examination, to apply them to mercury, or any substance whose coefficient of expansion is so widely different from that of a gas. A cursory glance at the tables of expansion will be sufficient, however, to show that the densest bodies have, in general, the least coefficients of expansion, so that the existence of such substances as mercury and the heavy metals, with their very small coefficients, encourages us to think that in such light and expansible liquids as ether, alcohol, etc., there may still be sufficient distance between the molecules to enable us to disregard their compressibility.

The ratio of the two products,  $JLD$  and  $E\epsilon T$ , which should be unity for an elementary substance containing only one atom to the molecule, I shall call the *principal ratio*. This ratio has not been determined for a single elementary substance.

From the mean results tabulated in § 3, we find for the principal ratio of alcohol the value 2.17; for ether, 0.74; for bisulphide of carbon, 0.89, and for turpentine, 0.93. These numbers are not probably accurate within five or even ten per cent., as two determinations of the modulus of elasticity alone are apt to differ by ten or twelve per cent.

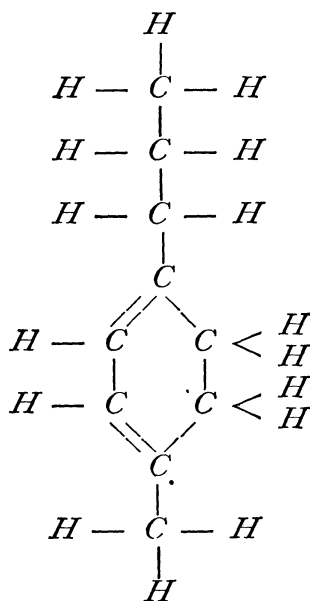
For bisulphide of carbon, we may adopt the graphical symbol  $S = C = S$ , the symbol  $S = S$ , or  $S \equiv S$ .



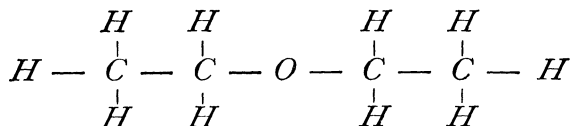
We shall find, in either case, one atom of carbon united to two atoms of sulphur; but in the first case the two sul-

phur atoms are attached only on one side, in the others there are two points of attachment, indicating clearly for each atom a loss of  $\frac{2}{10}$  of the maximum value of the latent heat, that is, a principal ratio of 0.90; but the first case indicates for two atoms the value 0.95 and for one the value 0.90, giving an average value anywhere from 0.91 to 0.94 according as we take the numbers of atoms, merely, or the atomic weights into account.

In the same way, for turpentine, assuming the graphical symbol



or some different symbol, more or less condensed,\* we have for the principal ratio a set of values from 0.83 to 0.90, and for ether



we have values from 0.84 to 0.91.

\* See Beilstein, Vol. II., page 1769.

In all these cases the attraction only of the atoms in direct union with a given atom is taken into account.

The calculated and observed values of the principal ratio are compared as follows:

	Calculated.	Observed.
Bisulphide of Carbon . . .	0.90 to 0.94	0.89
Turpentine . . . . .	0.83 to 0.90	0.93
Ether . . . . .	0.84 to 0.91	0.74

where it will be noticed that the calculated and observed values agree almost within the limit of probable error of the latter, according to a statement already made.

It was pointed out in the last section that a liquid might in some cases be treated as a mechanical mixture of two of its components, if the properties of these components were known.

We have for a mechanical mixture of  $A$  volumes of a liquid whose properties are designated by a prime ('), and  $B$  volumes of a liquid designated by two primes (''), the equations,

$$L = \frac{AL' + BL''}{A + B}$$

$$D = \frac{AD' + BD''}{A + B}$$

$$\epsilon = \frac{A\epsilon' + B\epsilon''}{A + B}$$

$$E = \frac{A + B}{\frac{A}{E'} + \frac{B}{E''}}$$

so that, if  $A + B = 1$ , we have

$$\frac{JLD}{E\epsilon T} = \frac{J(AL' + BL'')(AD' + BD'')}{E'E''(A\epsilon' + B\epsilon'')T},$$

$$\frac{JLD}{E\epsilon T} = \frac{J(AL' + BL'')(AD' + BD'')}{AE'' + BE'}.$$

in which formula we see that even if both liquids  $A$  and  $B$  satisfy the equations,

$$JL'D' = E'\epsilon'T, \text{ and } JL''D'' = E''\epsilon''T,$$

it will not in general be true that a mixture of the two liquids will do the same.

Treating alcohol as a mixture of ether and water we have, from the table in § 3, since

$$A = \frac{74}{92} \text{ and } B = \frac{18}{92},$$

the value 1.86 indicated\* for the principal ratio, at 0° centigrade, against 2.17 observed.

Independent of the theory, from a mechanical point of view, it may be interesting to note the values of the separate quantities indicated, namely: for the latent heat, 182, which is correct at 100° according to Zeuner; for the density, .787, which is true at about 25°; for the modulus of elasticity, 9,899,000,000, which would probably be right in the neighborhood of 35° (see Everett, page 52); and for the coefficient of expansion, .001196, which is the value at about 45° according to Pierre.

It is not inconsistent with the modern theories of molecular structure to suppose that those parts of different molecules which may have greater mutual cohesion than the rest should be drawn together so as to form a nucleus; and it is possibly the clustering of the "*hydroxyl*" radicals, in alcohol, which enables us to treat it so successfully as a mixture of ether and water. On the other hand, it is the impossibility, perhaps, of the formation of such nuclei that causes the approximate agreement of the first three liquids with the theory for elementary substances.

The investigation of the case of water, which alone remains, will be deferred until after the analytical treatment of

---


$$\frac{*JLD}{E\epsilon T} = \frac{42,000,000 \left( \frac{74}{92} 86.5 + \frac{18}{92} 575 \right) \left( \frac{74}{92} 0.736 + \frac{18}{92} \right)}{\frac{74}{92} 20,200,000,000 \times 8,800,000,000 \left( \frac{74}{92} 0.0015 - \frac{18}{92} 0.00005 \right) \times 273}$$


---

the coefficients of elasticity and of expansion; we shall find no reason to regard it as an exception to our fundamental laws.

In conclusion I would say that too much weight must not be attached to the accidental agreement of the three liquids tabulated, it being not very improbable that a fourth liquid should differ by a hundred per cent. from the value calculated in the same way. The case of alcohol is a good example, which has been explained. In dealing, however, with such large numbers as the elasticity and mechanical equivalent, and such small ones as the coefficient of expansion, the slightest mistake *in the formulæ* would be apt to increase or diminish the result by hundreds or perhaps millions of times; and even an approximate agreement between theory and observation must, in such cases, be considered in the light of a confirmation.

In the case, therefore, of the element bromine, the symbol being  $Br_2$ , I will venture to predict that the principal ratio will be found to be equal, very nearly, to 0.95. Since the total latent heat at  $63^\circ$  is given as 45.6 (Andrews), and the density 3.187 (Cooke), the coefficient of expansion at zero is .001038 (Pierre), and since the internal latent heat at  $0^\circ$  is 46.0,\* we have

$$E = \frac{42,000,000 \times 46.0 \times 3.187}{0.95 \times .001038 \times 273} = 22,870,000,000,$$

the same, nearly, as for water at  $41^\circ$  (Jamin), which value is therefore predicted for the coefficient of resilience of bromine to hold within the ordinary limits of errors of observation.

§ 6. If in the equation of equilibrium,

$$\bar{P} + P' + \bar{P}'' = 0,$$

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\* Calculated by the usual formulæ, assuming the absolute vapor density to be .007168 (reduced to  $0^\circ$  centigrade and 1,014,200 dynes pressure); also using the specific heats of the liquid and vapor as determined by Regnault.



we substitute the value of  $P'$  in terms of  $P'_0$  derived from equation I. § 2, namely,

$$\frac{P'}{P'_0} = \frac{T}{T_0} \frac{D}{D_0} \frac{l_0 - l}{l_0} \frac{l}{l - l'} = \frac{T}{T_0} \frac{l_0^2 (l_0 - l')}{l^2 (l - l')},$$

since the density varies inversely as the cube of any length, and if, moreover, we substitute the value of  $P''$  in terms of  $P''_0$ ,

$$\frac{P''}{P''_0} = \frac{l_0^6}{l^6},$$

as required by our hypothesis for bodies suffering no change of state, we have

$$\bar{P} + P_0 \frac{T}{T_0} \frac{l_0 (l_0 - l')}{l^2 (l - l')} + \bar{P}'' \frac{l_0^6}{l^6} = 0.$$

Differentiating with respect to  $\log V$ , and remembering that, since  $V : V_0 = l^3 : l_0^3$ ,

$\log V - \log V_0 = 3 \log l - 3 \log l_0$ , whence differentiating,  $-\frac{dV}{V} = \frac{3dl}{l}$ , we have

$$\begin{aligned} V \frac{d\bar{P}}{dV} + \frac{l}{3} \frac{dP'}{dl} + \frac{l}{3} \frac{d\bar{P}''}{dl} &= 0, \text{ that is,} \\ V \frac{d\bar{P}}{dV} - \frac{l}{3} P'_0 \frac{T}{T_0} \frac{l_0^2 (l_0 - l') (3l^2 - 2ll')}{l^4 (l - l')^2} \\ - \frac{l}{3} \frac{P'_0}{T_0} \frac{l_0^2}{l^2} \frac{(l_0 - l')}{(l - l')} \frac{VdT}{dV} - 6 \frac{l}{3} \bar{P}''_0 \frac{l_0^6 l^5}{l^{12}} &= 0. \end{aligned}$$

Simplifying, and substituting  $P'$  and  $P''$  in place of their values, also putting  $\bar{P} + P'$  in place of  $-\bar{P}''$ , we have

$$V \frac{d\bar{P}}{dV} - \frac{P'}{3} \left( \frac{4l' - 3l}{l - l'} \right) + P' \frac{V}{T} \frac{dT}{dV} + 2\bar{P} = 0. \text{ I.}$$

In this formula, if we suppose  $T$  constant, that is if  $\frac{dT}{dV} = 0$ , we find

$$V \frac{d\bar{P}}{dV} - \frac{P'}{3} \left( \frac{4l' - 3l}{l - l'} \right) + 2\bar{P} = 0;$$

but the coefficient of resilience,  $E$ , being defined as the limit of the numerical ratio of the increment of external pressure ( $\delta\bar{P}$ ) to the corresponding voluminal compression,  $\left( \frac{\delta V}{V} \right)$ , the temperature being constant, is equal algebraically to the first term  $V \frac{d\bar{P}}{dV}$ ; hence we have

$$E = \frac{P'}{3} \left( \frac{4l' - 3l}{l - l'} \right) - 2\bar{P}. \quad \text{II.}$$

Now if in I. we suppose the pressure to be constant, that is if  $\frac{dP}{dV} = 0$ , we shall have, transposing and inverting,

$$\epsilon = \frac{dV}{VdT} = \frac{P'}{T \left( \frac{P'}{3} \left( \frac{4l' - 3l}{l - l'} \right) - 2\bar{P} \right)} \quad \text{III.}$$

since  $\epsilon$  is defined as the coefficient of voluminal expansion under constant pressure.

The truth of the formulae II. and III. is easily tested by multiplying them together. We have

$$E\epsilon = \frac{P'}{T},$$

a relation already established by mechanical considerations (§2).

If, moreover, in III., we put  $\frac{l'}{l} = 0$ , and  $P + P' =$

—  $P'' = 0$ , that is, if we express the two conditions always assumed to hold in perfect gases, we shall have

$$\epsilon = \frac{1}{T}$$

as should be the case.\*

Substituting this value in the last equation, we find  $E = P'$ , which is easily shown to hold for perfect gases.

There is, therefore, every reason for confidence in the formulae of this section, the applications of which will be treated of when the ratio of  $l'$  to  $l$  has been determined.

The next and several following sections will be devoted to the relations which exist between the coefficients ( $E$  and  $\epsilon$ ) and their derivatives, which, we shall find, can be established independent of the value of  $l' \div l$ . It is sufficiently obvious, from the preceding investigation, that some such relations must exist; nevertheless these have not been studied, and have been known only empirically hitherto.

It is commonly supposed that in the experimental data for the expansion of liquids, or those at least which have been studied the most, little remains to be desired; such, however, is not the case, as may easily be seen by comparing the results of different observers. There is probably no branch of physics in which the accuracy attainable has been so far overestimated. Had the real uncertainty of the determinations been recognized, the theoretical bearings would undoubtedly have claimed more attention.

§ 7. To investigate the laws of a liquid or solid, expanding freely under heat, we put  $\bar{P} = 0$  in equation III. of the last section, which then becomes

$$\epsilon = \frac{3}{T} \frac{l - l'}{4l' - 3l} \quad \text{I.}$$

---

\* It may here, for convenience, be pointed out that  $\epsilon$  must not be confounded with the *absolute* coefficient of expansion, being defined approximately as the *ratio* of increase of volume to the volume itself for a rise of  $1^\circ$  in temperature. The difference, which is considerable for gases, in the case of liquids and solids will be found to be slight.

whence, by differentiation with respect to  $T$ ,

$$\begin{aligned}\frac{d\epsilon}{dT} &= -\frac{l-l'}{4l'-3l} \times \frac{3}{T^2} + \frac{3}{T} \left( \frac{(4l'-3l)+3(l-l')}{(4l'-3l)^2} \right) \frac{dl}{dT} \\ &= -\frac{\epsilon}{T} + \frac{3}{T} \left( \frac{1+\epsilon T}{4l'-3l} \right) \frac{dl}{dT}, \text{ from I., and substituting}\end{aligned}$$

for  $\frac{dl}{dT}$  its value,  $\frac{\epsilon l}{3}$  (see last section), we have

$$\begin{aligned}\frac{d\epsilon}{dT} &= -\frac{\epsilon}{T} + \frac{\epsilon l}{T(4l'-3l)} + \frac{\epsilon^2 l}{4l'-3l} \\ &= \frac{\epsilon}{T} \left( \frac{4(l-l')}{4l'-3l} \right) + \frac{\epsilon^2 l}{4l'-3l},\end{aligned}$$

hence again from I.

$$\frac{d\epsilon}{dT} = \frac{4\epsilon^2}{3} + \frac{\epsilon^2 l}{4l'-3l} = \frac{4\epsilon^2}{3} + \frac{\epsilon^2}{\frac{l'}{4}-3}.$$

Now from I. we have

$$\begin{aligned}4l'\epsilon T - 3l\epsilon T &= 3l - 3l'; \\ l'(4\epsilon T + 3) &= l(3\epsilon T + 3);\end{aligned}$$

$$\frac{l'}{l} = \frac{3+3\epsilon T}{3+4\epsilon T}; \quad \text{I.a.}$$

which, substituted in the preceding equations, gives

$$\frac{d\epsilon}{dT} = \frac{4}{3} \epsilon^2 + \frac{\epsilon^2}{\frac{12+12\epsilon T}{3+4\epsilon T} - 3} = \frac{4}{3} \epsilon^2 + \frac{\epsilon^2(3+4\epsilon T)}{3}$$

$$= \frac{4}{3} \epsilon^2 + \epsilon^2 + \frac{4}{3} \epsilon^3 T, \text{ so that, finally,}$$

$$\frac{d\epsilon}{dT} = \frac{7}{3} \epsilon^2 + \frac{4}{3} \epsilon^3 T, \quad \text{II.}$$

a relation between  $\epsilon$  and its first derivative which is independent of the value of  $l$  or  $l'$ .

Differentiating again, we find

$$\frac{d^2\epsilon}{dT^2} = \frac{14}{3} \epsilon \frac{d\epsilon}{dT} + 4\epsilon^2 T \frac{d\epsilon}{dT} + \frac{4}{3} \epsilon^3$$

where, substituting the value of  $\frac{d\epsilon}{dT}$  in terms of  $\epsilon$ , we have

$$\frac{d^2\epsilon}{dT^2} = 12.2\epsilon^3 + 15.5\epsilon^4 T + 5.3\epsilon^5 T^2. \quad \text{III.}$$

In the same way, by successive differentiation and substitution of the values of the first derivative in terms of  $\epsilon$ , we have

$$\begin{aligned} \frac{d^3\epsilon}{dT^3} = 101.11\epsilon^4 + 204.74\epsilon^5 T + 145.19\epsilon^6 T^2 \\ + 35.55\epsilon^7 T^3, \end{aligned} \quad \text{IV.}$$

accurate to two places of decimals, and

$$\begin{aligned} \frac{d^4\epsilon}{dT^4} = 1148.\epsilon^5 + 3218.\epsilon^6 T + 3504.\epsilon^7 T^2 + 1743.\epsilon^8 T^3 \\ + 332.\epsilon^9 T^4, \end{aligned} \quad \text{V.}$$

where the coefficients are expressed to the nearest unit; so that when  $\epsilon$  is given, the values of its successive derivatives at any temperature are determined.

At the end of this paper will be found a table (I.) showing the corresponding values of  $\epsilon$  and its first four derivatives at the freezing temperature of water ( $T_0 = 273^\circ$ ), from  $\epsilon_0 = .0001$  to  $\epsilon_0 = .002$ . Tables may easily be constructed for any temperature; the use of this particular table is explained below.

Let the volume ( $V$ ) of a liquid which is unity when the temperature is  $0^\circ$  centigrade ( $t = 0$ ) be represented by a sufficient number of coefficients in the form,

$$V = 1 + at + bt^2 + ct^3 + dt^4 + et^5 + \text{etc.};$$

then the absolute coefficient of expansion will be expressed by the series,

$$a + 2bt + 3ct^2 + 4dt^3 + 5et^4,$$

so that the voluminal expansion,  $\epsilon$ , which is the quotient of the absolute expansion by the volume, will be

$$\epsilon = \frac{a + 2bt + 3ct^2 + 4dt^3 + 5et^4 + \text{etc.}}{1 + at + bt^2 + ct^3 + dt^4 + et^5 + \text{etc.}}$$

whence, by actual division, we find

$$\begin{aligned} \epsilon = & a + (2b - a^2) t + (3c - 3ab + a^3) t^2 \\ & (+4d - 4ac - 2b^2 + 4a^2b - a^4) t^3 \\ & + (5e - 5ad - 5bc + 5a^2c + 5ab^2 - 5a^3b + a^5) t^4 \\ & + \text{etc.} \end{aligned} \quad \text{VI.}$$

Putting  $a', b', c', d'$  and  $e'$  in place of the coefficients of the successive powers of  $t$ , so that

$$\left. \begin{aligned} a' &= a \\ b' &= 2b - a^2 \\ c' &= 3c - 3ab + a^3 \\ d' &= 4d - 4ac - 2b^2 + 4a^2b - a^4 \\ e' &= 5e - 5ad - 5bc + 5a^2c + 5ab^2 - 5a^3b \\ &\quad + a^5 \end{aligned} \right\} \quad \text{VII.}$$

we have

$$\left. \begin{aligned} \epsilon &= a' + b't + c't^2 + d't^3 + e't^4 + \text{etc.} \\ \frac{d\epsilon}{dt} &= b' + 2c't + 3d't^2 + 4e't^3 + \text{etc.} \\ \frac{d^2\epsilon}{dt^2} &= 2c' + 6d't + 12e't^2 + \text{etc.} \\ \frac{d^3\epsilon}{dt^3} &= 6d' + 24e't + \text{etc.} \\ \frac{d^4\epsilon}{dt^4} &= 24e' + \text{etc.} \\ \frac{d^5\epsilon}{dt^5} &= 0 + \text{etc.} \end{aligned} \right\} \quad \text{VIII.}$$

Hence, substituting, we have

$$\frac{d^3\epsilon}{dt^3} = 6d' = t \frac{d^4\epsilon}{dt^4} \text{ etc., or } d' = \frac{1}{6} \frac{d^3\epsilon}{dt^3} - \frac{t}{6} \frac{d^4\epsilon}{dt^4} + \text{etc.}$$

$$\frac{d^2\epsilon}{dt^2} = 2c' + t \frac{d^3\epsilon}{dt^3} - t^2 \frac{d^4\epsilon}{dt^4} + \frac{t^3}{2} \frac{d^4\epsilon}{dt^4} + \text{etc.}$$

$$= 2c' + \frac{td^3\epsilon}{dt^3} - \frac{t^3}{2} \frac{d^4\epsilon}{dt^4} + \text{etc.,}$$

$$\text{whence } c' = \frac{1}{2} \frac{d^2\epsilon}{dt^2} - \frac{t}{2} \frac{d^3\epsilon}{dt^3} - \text{etc.}$$

$$\begin{aligned} \frac{d\epsilon}{dt} = b' + t \frac{d^2\epsilon}{dt^2} - t^2 \frac{d^3\epsilon}{dt^3} + \frac{t^3}{2} \frac{d^4\epsilon}{dt^4} + \frac{t^2}{2} \frac{d^3\epsilon}{dt^3} \\ - \frac{t^3}{2} \frac{d^4\epsilon}{dt^4} + \frac{t^3}{6} \frac{d^4\epsilon}{dt^4} - \text{etc.,} \end{aligned}$$

whence

$$b' = \frac{d\epsilon}{dt} - t \frac{d^2\epsilon}{dt^2} + \frac{t^2}{2} \frac{d^3\epsilon}{dt^3} - \frac{t^3}{6} \frac{d^4\epsilon}{dt^4} + \text{etc.,}$$

and finally

$$\begin{aligned} \epsilon = a' + t \frac{d\epsilon}{dt} - t^2 \frac{d^2\epsilon}{dt^2} + \frac{1}{2} t^3 \frac{d^3\epsilon}{dt^3} - \frac{t^4}{6} \frac{d^4\epsilon}{dt^4} \\ + \frac{t^2}{2} \frac{d^2\epsilon}{dt^2} - \frac{t^3}{2} \frac{d^3\epsilon}{dt^3} + \frac{t^4}{4} \frac{d^4\epsilon}{dt^4} + \frac{t^3}{6} \frac{d^3\epsilon}{dt^3} \\ - \frac{t^4}{6} \frac{d^4\epsilon}{dt^4} + \frac{t^4}{24} \frac{d^4\epsilon}{dt^4} + \text{etc.,} \end{aligned}$$

from which the value of  $a'$  can be determined.

Summing up our results, we have

$$\left. \begin{aligned} a' &= \epsilon - t \frac{d\epsilon}{dt} + \frac{t^2}{2} \frac{d^2\epsilon}{dt^2} - \frac{t^3}{6} \frac{d^3\epsilon}{dt^3} + \frac{t^4}{24} \frac{d^4\epsilon}{dt^4} - \&c. \\ b' &= \frac{d\epsilon}{dt} - t \frac{d^2\epsilon}{dt^2} + \frac{t^2}{2} \frac{d^3\epsilon}{dt^3} - \frac{t^3}{6} \frac{d^4\epsilon}{dt^4} + \&c. \\ c' &= \frac{1}{2} \left( \frac{d^2\epsilon}{dt^2} - t \frac{d^3\epsilon}{dt^3} + \frac{t^2}{2} \frac{d^4\epsilon}{dt^4} - \&c. \right) \\ d' &= \frac{1}{6} \left( \frac{d^3\epsilon}{dt^3} - t \frac{d^4\epsilon}{dt^4} + \&c. \right) \\ e' &= \frac{1}{24} \left( \frac{d^4\epsilon}{dt^4} - \&c. \right) \end{aligned} \right\} \text{IX.}^*$$

equations by which, at any temperature,  $t$ , the values of  $a'$ ,  $b'$ ,  $c'$ ,  $d'$  and  $e'$  may be calculated in terms of  $\epsilon$  and its derivatives, the relations between which have been already determined (I. to V.) The temperature specially adapted to this calculation is, however, the freezing temperature; for, putting  $t=0$  in equation IX. all but the first terms disappear.

It remains to be determined whether the successive terms in which  $\epsilon$  is expressed,

$$\epsilon = a' + b't + c't^2 + d't^3 + e't^4 + \text{etc.}$$

form a convergent series.

Referring to equations I.—V. we see that the  $n$ th derivative of  $\epsilon$  may be expressed

$$\frac{d^n \epsilon}{dT^n} = A\epsilon^{n+1} + B\epsilon^{n+2} T + \dots + X\epsilon^{2n+1} T^n,$$

---

\* It will be noticed that equations IX. are the expression of the *converse* of Maclaurin's theorem, from which they might have been derived by considering  $\epsilon$  as a constant, while  $a'$ ,  $b'$ , etc. are variables. Not being able at once to find a proof of the proposition in this form, it was thought advisable to give the calculation in full. The theorem is known as Bernoulli's. See Williamson's *Differential Calculus*, § 64.



hence

$$\begin{aligned} \frac{d^{n+1}\epsilon}{dT^{n+1}} &= A(n+1)\epsilon^n\left(\frac{7}{3}\epsilon^2 + \frac{4}{3}\epsilon^3 T\right) \\ &+ B\left(\epsilon^{n+2} + (n+2)\epsilon^{n+1}\left(\frac{7}{3}\epsilon^2 T + \frac{4}{3}\epsilon^3 T^2\right)\right) + \dots \\ &+ X\left(n\epsilon^{2n+1}T^{n-1} + (2n+1)\epsilon^{2n}\left(\frac{7}{3}\epsilon^2 T^n + \frac{4}{3}\epsilon^3 T^{n+1}\right)\right). \end{aligned}$$

The ratio of the term containing  $A$  in the  $n+1$ <sup>st</sup> derivative to the corresponding term in the  $n$ <sup>th</sup> derivative is

$$(n+1)\epsilon\left(\frac{7}{3} + \frac{4}{3}\epsilon T\right); \text{ that of the } B \text{ term is}$$

$$\frac{1}{T} + (n+2)\epsilon\left(\frac{7}{3} + \frac{4}{3}\epsilon T\right); \text{ that of the last term is}$$

$$\frac{n}{T} + (2n+1)\epsilon\left(\frac{7}{3} + \frac{4}{3}\epsilon T\right); \text{ so that the succes-}$$

sive derivatives ultimately form a divergent series.

Referring, however, to equation IX. we find

$$a' = \epsilon_0; \quad b' = \frac{d\epsilon_0}{dt}; \quad c' = \frac{1}{2} \frac{d^2\epsilon_0}{dt^2} \text{ etc.}$$

$$(n+1)' = \frac{1}{n!} \frac{d^n \epsilon_0}{dt^n}$$

$$(n+2)' = \frac{1}{(n+1)!} \frac{d^{n+1} \epsilon_0}{dt^{n+1}}$$

so that the ratio of the  $(n+2)$ <sup>d</sup> to the  $(n+1)$ <sup>st</sup> term in the series,

$$\begin{aligned} \epsilon &= a' + b't + c't^2 + d't^3 + e't^4 + \dots + n't^{n-1} \\ &+ (n+1)'t^n + (n+2)'t^{n+1} + \text{etc.}, \end{aligned}$$

will be

$$\frac{(n+2)'}{(n+1)'} t = \frac{t}{n+1} \frac{d^{n+1}\epsilon_0}{d^n \epsilon_0}$$

The last factor can be represented as the quotient of two sums, each of a number of terms; the ratio of no term in the numerator to the corresponding term in the denominator can by any possibility exceed

$$\frac{n}{T} + (2n + 1) \epsilon \left( \frac{7}{3} + \frac{4}{3} \epsilon T \right),$$

so that the value of the quotient must be less than this quantity. Hence the ratio of the  $(n + 2)^d$  term to the  $(n + 1)^{st}$  in the expansion of  $\epsilon$  cannot exceed the value

$$\frac{t}{n + 1} \left( \frac{n}{T} + (2n + 1) \epsilon \left( \frac{7}{3} + \frac{4}{3} \epsilon T \right) \right)$$

When  $n$  becomes indefinitely large, this ratio approaches the value  $\frac{t}{T} + 2\epsilon t \left( \frac{7}{3} + \frac{4}{3} \epsilon T \right)$ , so that if

$\frac{t}{T} + 2\epsilon t \left( \frac{7}{3} + \frac{4}{3} \epsilon T \right) < 1$ , the series is certainly convergent.

Now  $t$  is necessarily less than  $T$ , since  $T^\circ = 273^\circ + t$ ; and the smaller the value of  $\epsilon$ , the greater can be the ratio of  $t$  to  $T$  without invalidating the convergence of the series.

If  $t \leq 0$ , evidently  $\epsilon_0$  can be as great as one pleases, that is, the series is necessarily convergent for a descending scale of temperature.

If  $t \leq 60^\circ$  and  $\epsilon < .002$

we have  $2\epsilon t \left( \frac{7}{3} + \frac{4}{3} \epsilon T \right) < \frac{5}{6} < 1 - \frac{t}{T}$ ; hence the tables, which were constructed from  $\epsilon = .0001$  to  $\epsilon = .0020$ , are at least reliable up to  $60^\circ$ .

In the same way  $\epsilon$  is certainly determinate up to the value .00135 for at least  $90^\circ$ ; and for still smaller values of  $\epsilon_0$ , still higher temperatures may be used. It will be noticed that there is no liquid whose coefficient of expansion is as great as .002 which does not boil, at the ordinary pressure, below  $60^\circ$ ; and none boiling above  $90^\circ$  has a greater coefficient than .00135, so that thus far theory and fact are not at variance. It must also be remembered that the ratio of a term to the one preceding it was shown

to be less than  $\frac{t}{T} + 2\epsilon t \left( \frac{7}{3} + \frac{4}{3}\epsilon T \right)$  by assuming that the maximum ratio of the corresponding coefficients held for all. Since this is evidently not the case, the series is much more convergent than has been assumed, and there is every reason to believe that the value of  $\epsilon$  is determinate for all temperatures below a certain critical point. Such a point is now believed to exist for all substances, above which the laws of liquid expansion will cease to apply. The correspondence of theory and fact in respect to this point will, if established, afford a complete physical demonstration of the sufficient convergence of our series.

The value of the critical temperature we are not yet prepared to calculate, owing to the difficulty of the mathematical solution; but in one of the sections following we shall see how it may be derived from our theory in a much more simple way.

It remains, therefore, to conclude that, since  $\epsilon$  is determinate for all points below the critical temperature, the volume and its coefficients must also be determinate, and their calculation by means of the derivatives in Table I. is therefore perfectly legitimate.

Equations VII. enable us to determine the value of  $a$ ,  $b$ ,  $c$ ,  $d$  and  $e$ , successively, for all values of  $\epsilon$  at the temperature zero; and a table will be found at the end of the paper (II.) in which these coefficients are calculated for values of  $\epsilon_0$  from .0001 to .0020.

By means of these coefficients, a volume table has been constructed (III.) by which, when the value of  $\epsilon_0$  is known, the volume may be found, calculated at intervals of  $10^\circ$ , from  $-10^\circ$  to  $150^\circ$  centigrade, the volume at zero being unity; and furthermore, by means of this table, if the volume be known at any temperature besides zero, the value of  $\epsilon_0$  and hence the volume at any other temperature may be deduced.

If, moreover, only the ratio of expansion be known for a given range of temperature, it will be possible to find by trial what value of  $\epsilon_0$  will account for this ratio, and thus to determine completely the laws of expansion of the substance.

The advantage of this method of treating expansion, which requires for substances not subject to a change of state only a single accurate observation in place of at least three, and which is the same for all bodies having the fundamental coefficient in common, is obvious; it remains only to see how closely our calculations are borne out by experience.

§ 8. The usual method of determining the law of expansion of a substance depends upon the assumption that the volume at any temperature,  $t$ , can be expressed sufficiently well by three constant coefficients,  $A$ ,  $B$ ,  $C$ , in the form

$$V = 1 + At + Bt^2 + Ct^3.$$

Four observations of the volume are usually made at different temperatures, the first being preferably zero, or, when that is impossible, the melting point. The other three, in absence of the data, may be assumed to have been chosen at equal intervals up to the boiling point, or the highest temperature observed. It is then always possible to assign such values to  $A$ ,  $B$  and  $C$  as shall make the volumes calculated by the formula agree with those observed at all four temperatures. The values of the coefficients,  $A$ ,  $B$  and  $C$ , as determined by Kopp and Pierre, have been tabulated by Sharples for about eighty-eight liquids, of which eleven were determined by both observers. In order to compare our results most directly with their figures, we must calculate the theoretical values of  $A$ ,  $B$  and  $C$  which would represent the volumes correctly according

to Table III. at four different temperatures which may divide the whole range of temperature in question into three equal parts.

We have, for  $0^\circ$  and any three temperatures,  $t_1$ ,  $t_2$  and  $t_3$ , at which the formulae must hold, the simultaneous equations:

$$V_0 = 1,$$

$$V_1 \begin{cases} = 1 + At_1 + Bt_1^2 + Ct_1^3 \\ = 1 + at_1 + bt_1^2 + ct_1^3 + dt_1^4 + et_1^5 + \text{etc.} \end{cases} \begin{matrix} (1) \\ (2) \end{matrix}$$

$$V_2 \begin{cases} = 1 + At_2 + Bt_2^2 + Ct_2^3 \\ = 1 + at_2 + bt_2^2 + ct_2^3 + dt_2^4 + et_2^5 + \text{etc.} \end{cases} \begin{matrix} (3) \\ (4) \end{matrix}$$

$$V_3 \begin{cases} = 1 + At_3 + Bt_3^2 + Ct_3^3 \\ = 1 + at_3 + bt_3^2 + ct_3^3 + dt_3^4 + et_3^5 + \text{etc.} \end{cases} \begin{matrix} (5) \\ (6) \end{matrix}$$

Subtracting (2) from (1), (4) from (3), and (6) from (5), transposing in each case  $(A - a)t$ , and dividing by  $t$ , we have

$$A - a = - (B - b) t_1 - (C - c) t_1^2 + dt_1^3 + et_1^4 + \text{etc.} \quad (7)$$

$$A - a = - (B - b) t_2 - (C - c) t_2^2 + dt_2^3 + et_2^4 + \text{etc.} \quad (8)$$

$$A - a = - (B - b) t_3 - (C - c) t_3^2 + dt_3^3 + et_3^4 + \text{etc.} \quad (9)$$

Subtracting (8) from (7) and (9) from (8) we have, transposing and dividing by  $t_2 - t_1$  and  $t_3 - t_2$ , respectively,

$$(B - b) = - (C - c) (t_2 + t_1) + d (t_2^2 + t_2 t_1 + t_1^2) + e (t_2^3 + t_2^2 t_1 + t_2 t_1^2 + t_1^3) + \text{etc.} \quad (10)$$

$$(B - b) = - (C - c) (t_3 + t_2) + d (t_3^2 + t_3 t_2 + t_2^2) + e (t_3^3 + t_3^2 t_2 + t_3 t_2^2 + t_2^3) + \text{etc.} \quad (11)$$

Subtracting (11) from (10), transposing and dividing by  $(t_3 - t_1)$ , we have

$$C - c = d (t_3 + t_2 + t_1) + e (t_3^2 + t_2^2 + t_1^2 + t_3 t_2 + t_3 t_1 + t_2 t_1) + \text{etc.} \quad (12)$$

Hence for any three temperatures,  $t_1$ ,  $t_2$  and  $t_3$ , at which the two formulae are assumed to agree, we can find the difference between  $C$  and  $c$ , and hence by substitution in (10) or (11) the value of  $B - b$ , which again, substituted in (7), (8) or (9), will give the excess of  $A$  over  $a$ .

If, however, the three temperatures,  $t_1$ ,  $t_2$  and  $t_3$ , are chosen at equal distances, as we presume in absence of contrary evidence that they are, we have  $t_2 = 2t_1$  and  $t_3 = 3t_1$ ;

$$\left. \begin{aligned} C &= c + 6dt + 25et^2 + \text{etc.} \\ B &= b - 11dt^2 - 60et^3 + \text{etc.} \\ A &= a + 6dt^3 + 36et^4 + \text{etc.} \end{aligned} \right\} \text{ I.}$$

where  $t$  is the lowest of the three temperatures at which the formula is exactly fulfilled.

Table IV. was constructed to show the different values of  $A$ ,  $B$  and  $C$  corresponding to values of  $\epsilon$  from .0001 to .0020, which must be chosen to represent correctly the volume at the extremes of three adjacent intervals of temperature, each equal to the figure at the head of the column, the lowest extreme being (strictly) zero. The table shows that the values of  $B$  and  $C$  may be very different according to the range of temperature chosen, and that  $A$  cannot be relied upon to represent the true coefficient of expansion at zero. As a practical confirmation of this indication of the theory, I will quote three different values of  $A$  for butyrate of ethyl, namely, .001202790, from  $13^\circ$  to  $99^\circ$ , and .000632742, from  $99^\circ$  to  $119^\circ.4$ , according to Pierre, while Kopp gives .00117817, probably for the whole range of temperature. It would seem, at first sight, impossible that two such careful observers could have differed by 50% in their estimation of the coefficient  $A$  from  $99^\circ$  to  $119^\circ$ , but if we compare the volumes indicated in each case, taking into account the other coefficients as well, we shall find differences which may easily be attributed to errors of observation.\* The fact remains

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\* See Table VII.

that we cannot rely on these coefficients for the expansion at any temperature, however accurate the volumes may be. Before proceeding to a comparison of the results of our theory with those of observation, let us examine a little more closely into the probable error of the latter. The example quoted is an extreme case, and we will give Pierre the advantage of choosing the nearest of his two coefficients  $A$ , for comparison, thus considerably reducing the difference between the two observers; let us, moreover, take the mean of the coefficients in the case of fusel-oil and butyric acid, by which the agreement will be still further increased; we shall find nevertheless between Kopp and Pierre (by the method of squaring the errors), in the eleven liquids which they have determined in common, a mean difference for the coefficient  $A$  of .0000489 + (between four and five per cent.), for the coefficient  $B$  a mean difference of .000001318 + (nearly fifty per cent.) and for the coefficient  $C$  a mean difference of .00000001345 + (between sixty and seventy per cent. of the average value of the coefficient).

The details of the calculation are embodied in Table V., in which the figures of Kopp and Pierre are quoted in full from Sharples. It is thought that the figures will not need explanation.

§ 9. We are now prepared to make a direct comparison of theory and observation. Table VI. contains the values of  $A$ ,  $B$  and  $C$  calculated and observed for 75 liquids, which may be identified by means of the numbers following their name and symbol in Table XVIII. It was not thought necessary to include in Table VI. the eleven liquids alluded to in the last section, as they are to be subjected to a much severer test. Besides these, the only two omitted from the table were sulphurous dioxide, which was out of the reach of the volume table, and is hardly a

liquid, and phosphorous chloride, which has a coefficient  $C$  some thousand times greater than the average (no other liquid exceeding it by more than seven times), thus clearly implying that this substance is an exception, like water, to the general law of expansion.\*

We shall see that the existence of such exceptions does not militate, in any way, against the truth of our theory.

In the construction of Table VI. the calculated values of  $A$ ,  $B$  and  $C$  were taken by interpolation from Table IV. so as to represent, as correctly as possible, both the volume and coefficient of expansion of the liquid, between  $0^\circ$  and the boiling point, using of course the table calculated for the given range of temperature.

The observed values are taken directly from Sharples' Tables, omitting however several figures which we have proved to be insignificant; when two values, not differing greatly, were given for different ranges of temperature, the mean was taken. The influence upon the result would in no case be perceptible.

The differences are given for the three coefficients  $A$ ,  $B$  and  $C$ , calculated and observed; and it will be found that the mean difference for  $A$  being only .000,003,3, that for  $B$  is .000,001 +, and that for  $C$ , throwing out number 74, is .000,000,012 +, which we see in all cases is less than the mean difference between the two observers already found in the case of the eleven liquids which they determined in common.

It is proposed to subject these eleven liquids to a still more searching examination. At intervals of  $10^\circ$ , by aid of the empirical formula,

$$V = 1 + At + Bt^2 + Ct^3$$

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\* The probability of an error, by chance, exceeding the probable error, as in this case, by more than a hundred times was too small to be included in the tables of Chauvenet or in those of Haskell which are appended.



the volume, from  $0^{\circ}$  (or else the melting point) up to the boiling point in each liquid, has been calculated both according to Pierre and according to Kopp. These values will be found in Tables VII., in the columns headed  $V_P$  and  $V_K$  respectively.

The mean was then taken in the column  $V_{P,K}$ , and the difference between Kopp and Pierre, in the column headed  $\Delta_{P-K}$ , is squared in the next column,  $\Delta^2$ .

With the method of least squares, by actual trial, the best value of  $\epsilon$  in Table III. was found, to represent the volume through the same range of temperature. The value of  $\epsilon$  is given at the head of the table, and the volumes, taken from Table III. by interpolation, are in the column  $V_{\epsilon}$ . The differences between these and the mean volumes, according to Kopp and Pierre, are given in the column  $\Delta_{P,K-\epsilon}$ , and the squares are given in the last column,  $\Delta^2$ .

These columns of squares are added for each liquid, so that the sum of all the squares may easily be found.

Amongst this number, or amongst the seventy-five previously examined, if there be a single liquid (as for instance butyric acid) in which a molecular change affecting the volume is brought about by heat, the mean difference between theory and observation will be indefinitely increased; if there be the slightest *constant* error in the observation, the elimination of which is impossible, the observations will be equally accordant, but the theory will seem *unduly* to disagree; in all cases, the mean square of the difference between theory and observation will be increased by the sum of the mean squares of the errors from each source.

There is no reason to suppose that the constants of the standards, in terms of which the expansion was expressed, as, for instance, the coefficients of expansion of mercury and glass, determined by Regnault, were more accurately

measured than any of the rest, being equally subject to thermometric error; if this be true, then, according to the theory of probability, the mean error of the results of Kopp and Pierre combined will be, not one-quarter of their mean difference, as would be the case if the standards were absolutely reliable, but one-half or three-quarters, according as we assign to Regnault (or whatever standard they may have used) the weight of two observers or that of only one.

Where, as in the present case, the mean difference of theory and observation is equal to about two-thirds of the mean difference of two observers, the discrepancy is probably due to errors of observation. It would appear that for ten out of the eleven liquids most closely examined,—the exception being butyric acid—the agreement is actually greater than probability could require even if the theory (as well as the standards) were known to be absolutely true.

In the case of solids, according to the results obtained by Dr. Matthiessen, the law of expansion will need to be modified. I have already pointed out that if the molecule or atom were itself compressible, the indication of the kinetic theory would not be strictly fulfilled; the departure can easily be subjected to mathematical computation, and its value determined, constantly increasing with the state of aggregation.

It appears to me, however, that the facts do not justify such a laborious calculation. It is to be observed that in weighing in water, as in the experiments of Dr. Matthiessen, any error in the determination of the density of the water,\* or of its temperature, will affect the results by a proportionate amount.

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\* The mean difference between Kopp and Pierre for water [see Table, Sharples, page 73] is a little more than .0005, or one-twentieth of one per cent., corresponding to an error of one-tenth of one degree in temperature.

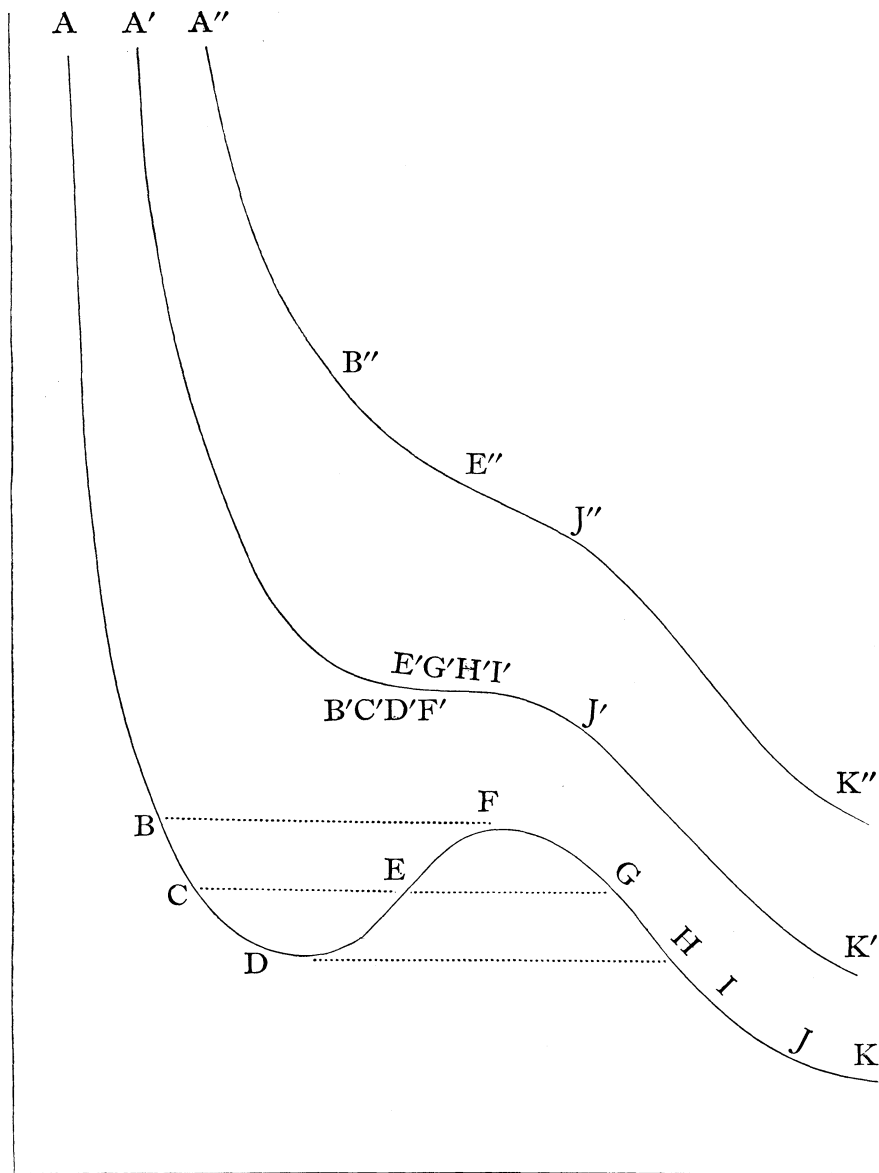
In conclusion, concerning *all* the results which have been brought forward (which are the best that I have been able to find) I would suggest that until we discover some more accurate method of measuring temperature than we at present possess, it will be useless to hope to obtain in any thermometric measurement of the rates of change of expansion more than an approximation to the truth.

It is therefore absurd to base a theory even upon such precise measurements as those of Dr. Matthiessen. The atoms are undoubtedly compressible, but we shall be unable to obtain a measure of their compressibility in this way, and we have no reason thus far to suppose that the theory of expansion, developed for the lighter liquids, is not applicable, without modification, to solids.

The result of the investigation suggests that the treatment of matter in its different states may differ only in that here, one factor, there, another, can in practice be neglected; and that the Laws of Expansion are fundamentally the same for all bodies, whether they be solid or liquid, vapor or gas.

§ 10. Maxwell has pointed out in his *Theory of Heat*, chapter V., page 107, that the elasticity of a fluid is expressed by the quotient of the *slope* of a curve by the *volume*, which is its abscissa, while the ordinate is the pressure. Hence if the volume be unity, the slope and elasticity are equal. The present section is devoted to the analytical investigation of elasticity and its application to isothermal curves.

"It has been suggested by Professor James Thomson" (see Maxwell, chapter VI., page 124), "that the isothermal curves" [of liquids in contact with their vapors] "for temperatures below the critical temperature are only apparently, and not really, discontinuous, and that their true form is somewhat similar in its general features to the curve *ABCDEFGHJK*."



"The peculiarity of this curve is that between the pressures indicated by the horizontal lines,  $BF$  and  $DH$ , any horizontal line, such as  $CEG$ , cuts the curve in three different points. One of these, indicated by  $C$ , evidently corresponds to the liquid state. Another, indicated by  $G$ , corresponds to the gaseous state."

Maxwell continues to the effect that  $E$  may be left out of consideration, being a point of unstable equilibrium.

Curves are also given of the general form  $A'B'C'D'E'F'G'H'K'$  and  $A''B''E''J''K''$ , representing isothermals at and above the critical temperature. All these curves are concave upward as far as a certain point, such as  $E$ , then convex as far as  $J$ , and finally concave again. The slope of all is at first downwards, and finally downwards. Below a certain isothermal, the concave curvature is sufficient to cause an upward slope between  $D$  and  $F$ ; above it, it is insufficient; and this particular isothermal is characterized by having a slope which reaches zero as its limit and then tends downward again. Now unless the curvature changed its sign at the point where the curve becomes horizontal, the slope on one or the other side of this curve would be upward; hence we may determine this curve by supposing the slope and curvature to be equal simultaneously to zero. It is evident, moreover, that this is a complete definition of the curve, since no other can at any point fulfil the same conditions.

It is hardly necessary to add that this isothermal belongs to what is called the "critical temperature." Below it, since at  $E$  the slope is upward, there can always be found for a given pressure two volumes,  $C$  and  $G$ , at which the substance is in stable equilibrium. Above it, since the slope is always downwards, only one state is possible. That is, the temperature of this isothermal is the limit up to which a liquid is possible in contact with its vapor.

The method of treating isothermals and determining the critical temperature by the theory is extremely sim-

ple. We have merely to put the elasticity which we have found in § 6, II.,

$$E = \frac{P'}{3} \left( \frac{4l' - 3l}{l - l'} \right) - 2 \bar{P},$$

and its derivative with respect to the volume, or  $l$ , which amounts to the same thing, simultaneously equal to zero. We shall first find an expression for the ratio of  $l'$  to  $l$ , *in the critical state itself*, which will enable us to calculate successively the cohesive, the internal, the external pressures, the density and the critical temperature, which latter, being found for one point of the curve, is the same of course for all. These are all the constants which we need to determine.\*

The formula for the elasticity may also be written, since  $\bar{P} + P' + \bar{P}'' = 0$ ,

$$E = \frac{P'}{3} \left( \frac{3l - 2l'}{l - l'} \right) + 2\bar{P}'', \text{ whence, substituting the}$$

values of  $P'$  and  $P''$  in terms of  $P'_0$  and  $P''_0$ ,

$$\begin{aligned} E &= \frac{P'_0}{3} \frac{l_0^2}{l^2} \frac{(l_0 - l')}{(l - l')} \frac{T}{T_0} \frac{(3l - 2l')}{(l - l')} + 2 P''_0 \frac{l_0^6}{l^6} \\ &= \frac{P'_0}{3} \left( \frac{l_0^2}{l^2} \frac{l_0 - l'}{l - l'} \frac{T}{T_0} \frac{3l - 2l'}{l - l'} - 6 \frac{l_0^6}{l^6} \left[ 1 + \frac{\bar{P}_0}{P'_0} \right] \right) I. \end{aligned}$$

Differentiating with respect to  $l$ , and remembering that all other factors are constant, we have

$$\frac{dE}{dl} = \frac{P'_0}{3} \left\{ \begin{aligned} &\frac{3l^2 (l - l')^2 l_0^2 (l_0 - l') T}{l^4 (l - l')^4 T_0} \\ &- \frac{2(l^2(l - l') + l(l - l')^2)l_0^2(l_0 - l')(3l - 2l') T}{l^4 (l - l')^4 T_0} \\ &+ 36 \frac{l_0^6}{l^7} \left[ 1 + \frac{\bar{P}_0}{P'_0} \right] \end{aligned} \right\}$$

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\* The elasticity being zero, the coefficient of expansion will be indefinitely great at that point; the latent heat will disappear, and instead we shall find an enormous specific heat under a sufficiently great constant pressure, falling off rapidly as the temperature is increased. The surface tension is very closely related to the cohesive pressure, and the distinction between vapor tension and external pressure disappears.

$$\frac{dE}{d \log l} = \frac{P'_0}{3} \left( 36 \frac{l_0^6}{l'^6} \left[ 1 + \frac{\bar{P}_0}{P'_0} \right] - \frac{l_0^2 (l_0 - l')}{l'^2 (l - l')} \frac{T}{T_0} \frac{[(3l - 2l')^2 + ll']}{(l - l')^2} \right) \text{II}$$

The left hand term in the parenthesis is essentially positive; the right hand term essentially negative, since  $l > l' > 0$  and  $l_0 > l'$ . When  $l$  becomes very great, the left hand term disappears in comparison with the other; as  $l - l'$  approaches zero the right hand term becomes infinite, so that at both extremes the curvature is concave upwards. Between the two, it is evident that, if  $\frac{T}{T_0}$  is

sufficiently small, the right hand term will become less than the left hand, and the curvature will become convex upward. There will therefore in general be two middle points where the curve is perfectly straight.

From I. we see that when  $l = l'$ ,  $E = \infty$ , that is, the curve becomes parallel to the axis of pressures with an infinite downward slope; when  $l$  increases indefinitely, the curve approaches the axis of volumes as an asymptote, and the slope becomes positive before it vanishes owing to the disappearance of the second term in parenthesis in comparison with the first. Between these values, if  $\frac{T}{T_0}$  is sufficiently small, the slope evidently becomes

negative somewhere, and in changing to negative and then to positive again, must twice pass through the value zero. Hence there will be in general two points,  $D$  and  $F$ , where the curve is parallel to the axis of volumes. When, however,  $T$  is increased, it is at last impossible for the slope to become negative; there must be some value for  $T$  when the slope reaches the value zero without crossing it; for we may put  $E$  and its derivative simultaneously equal to zero, and the isothermal in question fulfils all the conditions which should hold at the critical temperature.

It is easy to show that all the curves in the neighborhood of the critical temperature have the general charac-

teristics which were anticipated by Professor Thomson; and to prove by a second differentiation, as well as by actually plotting these curves, that the elasticity and its derivative do not more than twice pass through the value zero. We have, therefore, every reason to expect that the true form of the equation may have been found for the curves whose characteristics were predicted thirteen years ago.

If we suppose equations I. and II. to be simultaneously equal to zero, we have, multiplying I. by 6, dividing both equations by  $\frac{P'_0}{3}$ , and transposing,

$$\frac{6l_0^2(l_0 - l')}{l'^2(l - l')} \frac{T}{T_0} \frac{(3l - 2l')}{(l - l')} = \frac{36l_0^6}{l'^6} \left[ 1 + \frac{\bar{P}_0}{P'_0} \right]$$

$$\frac{l_0^2}{l'^2} \frac{(l_0 - l')}{(l - l')} \frac{T}{T_0} \frac{(3l - 2l')^2 + ll'}{(l - l')^2} = \frac{36l_0^6}{l'^6} \left[ 1 + \frac{\bar{P}_0}{P'_0} \right]$$

whence

$$\frac{6l_0^2}{l'^2} \frac{(l_0 - l')}{(l - l')} \frac{T}{T_0} \frac{(3l - 2l')}{(l - l')} = \frac{l_0^2}{l'^2} \frac{(l_0 - l')}{(l - l')} \frac{T}{T_0} \frac{(3l - 2l')^2 + ll'}{(l - l')^2}$$

Clearing of fractions and common factors,

$$6(l - l')(3l - 2l') = (3l - 2l')^2 + ll'$$

$$18l^2 - 12ll' - 18ll' + 12l'^2 = 9l^2 - 12ll' + 4l'^2 + ll'$$

$$9l^2 - 19ll' + 8l'^2 = 0$$

$$l^2 - \frac{19}{9} ll' + \left(\frac{19}{18}\right)^2 l'^2 = \left(\frac{19}{18}\right)^2 l'^2 - \frac{8}{9} l'^2$$

$$\frac{l}{l'} = \frac{19}{18} \pm \sqrt{\left(\frac{19}{18}\right)^2 - \frac{8}{9}}$$

Since  $l$  is essentially greater than  $l'$ , only the positive root is to be taken, and we have, finally, in the critical state, the condition,

$$\frac{l}{l'} = 1.53022$$

III.



Substituting this value in the equation

$$E = \frac{P'}{3} \left( \frac{3l - 2l'}{l - l'} \right) + 2 \bar{P}'' = 0, \text{ we have}$$

$$\frac{P'}{P''} = 1.228, \text{ nearly, whence}$$

$$\frac{P}{P''} = 0.228, \text{ nearly.}$$

$$\text{Substituting for } P'' \text{ its value, } P_o'' \frac{l_o^6}{l'^6} = P_o'' \left( \frac{l_o}{l'} \right)^6 \left( \frac{l'}{l} \right)^6$$

$$P' = 0.09566 \left( \frac{l_o}{l'} \right)^6 P_o'' \quad \text{IV.}$$

$$P = 0.01776 \left( \frac{l_o}{l'} \right)^6 P_o'' \quad \text{V.}$$

The last expression was obtained by taking the difference of two very nearly equal values, and is therefore not very reliable. If the atoms are spherical, the apparent molecular diameter (or shortening of the free path) will be less, the further the molecules are apart; in a linear expansion, therefore, of from forty to fifty per cent., we must on this account look for a greater free path, and consequently a less kinetic pressure; furthermore, since for great distances the law of variation of the magnetic attraction is inversely as some power much greater than the fourth, and we have supposed that the average power is the fourth, it follows that at short distances the attraction, according to the analogy, cannot vary quite so rapidly. Both these causes combined would tend to diminish the external pressure, the first by lessening the frequency of impact of the molecules (or atoms), the second by holding them more closely together; the result is that we must expect to find that the external pressure, calculated in this way, is considerably too great.

By inspection of the figures given, it will be seen that a combined variation of about twenty per cent. in these two pressures would annihilate completely the external pressure; hence if the observed values lie between zero and those calculated, the total error due to disturbing causes cannot exceed twenty per cent.

For the critical temperature,  $T_1$ , we have from §2, I. (see §.6, init.) the formula,

$$P' = P_o' \left( \frac{l_o^2}{l^2} \frac{(l_o - l')}{(l - l')} \frac{T}{T_o} \right)$$

$$\text{Hence } \frac{T_1}{T_o} = \frac{P'_1}{P_o'} \frac{l_1^2 (l_1 - l')}{l_o^2 (l_o - l')}$$

$$= 0.09566 \left[ \frac{l_o}{l'} \right]^3 \frac{P_o''}{P_o'} (1.5302)^2 (.5302) \frac{l_o}{l_o - l'}$$

or, finally,

$$\frac{T_1}{T_o} = .11876 \left( \frac{l_o}{l'} \right)^3 \frac{P_o''}{P_o'} \frac{l_o}{l_o - l'} \quad \text{VI.}$$

an equation by which the value of the critical temperature may be determined when we know at any temperature  $T_o$  the ratio of  $l'$  to  $l_o$ . We have seen reason to expect that our formulae are to be relied upon within ten or twenty per cent. and shall hope to find, accordingly, later on, that the values of the critical temperature, calculated by this formula, are sufficiently close to those estimated by Cagniard de la Tour.

§ 11. The surface tension of a liquid is very easily determined by means of the height to which it will rise in a capillary tube, of known diameter, which it thoroughly wets. It is believed that the surface tends to contract with a perfectly measurable force, not depending upon the depth of the liquid, but being the same for the thin-

nest possible film (in a soap-bubble for instance), as in the surface of deep water. The contractile force depends, accordingly, upon the breadth of the film, and not on its thickness; and in Everett's *Units and Physical Constants* (page 42, § 46) we find the tension in dynes of a surface a centimetre broad. Since a film has two surfaces, each with a tension independent, nearly, of the thickness as assigned, to produce a given film would require a perfectly measurable quantity of work, which, in the thinnest possible films, must be a considerable fraction of that necessary to convert the liquid into vapor.

This fraction is easily determined theoretically. For the latent heat, instead of the series,

$$12 \left( 1 + \left(\frac{1}{2}\right)^2 + \left(\frac{1}{3}\right)^2 + \left(\frac{1}{4}\right)^2 + \text{etc.} \right)$$

which represents the equivalent of the total number of atoms from which a given atom has to be separated, we now have only

$$6 \left( 1 + \left(\frac{1}{2}\right)^3 + \left(\frac{1}{3}\right)^3 + \left(\frac{1}{4}\right)^3 + \text{etc.} \right)$$

the molecules all lying in one plane. From each of these must be subtracted, as before, the equivalent of the number of atoms which remain clinging to a given atom in the state of vapor. The value of the last series, which is the more convergent of the two, is easily found to be 7.206, which, subtracted from the first series, or 19.740, leaves 12.534 to represent the work done in stretching the film.

Hence the fraction of the work spent in this way is  $\frac{12.534}{K(19.740)}$ , or for ordinary liquids about two-thirds of that required for complete vaporization.

It is therefore easy, if we know the principal ratio,  $K$ , to find the thickness of the thinnest possible film. To generate each square centimetre of such a film, the tension

( $S$ ) of each surface must be overcome through the distance of one centimetre, requiring an expenditure of energy equal numerically to twice this tension; the density of the film being  $D$  and the thickness  $l$ , the weight will be  $lD$  and the equivalent of the internal latent heat  $JlD$ , about two-thirds of which is required to *laminate* the liquid in this way. Equating the two expressions for the work, we have  $\frac{12.534 J l D}{(19.740) K} = 2 S$ , whence

$$l = \frac{3.15 KS}{J l D}, \quad \text{II.}$$

a formula by which the absolute thickness of a molecular film may be calculated according to the theory.\*

If we could regard the cohesive pressure across a square centimetre of surface as the sum of the contractile forces of a sufficient number of films of thickness  $l$ , and cutting the surface at right-angles, we should at once obtain an expression for the cohesive pressure; but we must remember to take into account the effect of oblique action, and the accumulative attraction of successive shells, which will increase the results in the ratio of the two series, (1) and (2),

$$\begin{aligned} (1) \quad & 1 + \left(\frac{1}{2}\right)^3 + \left(\frac{1}{3}\right)^3 + \left(\frac{1}{4}\right)^3 + \text{etc.} \\ & + \left(\frac{1}{2}\right)^3 + \left(\frac{1}{3}\right)^3 + \left(\frac{1}{4}\right)^3 + \text{etc.} \\ & + \left(\frac{1}{3}\right)^3 + \left(\frac{1}{4}\right)^3 + \text{etc.} \\ & + \left(\frac{1}{4}\right)^3 + \text{etc.} \\ & + \text{etc.} \end{aligned}$$

$$\begin{aligned} (2) \quad & 1 + \left(\frac{1}{2}\right)^4 + \left(\frac{1}{3}\right)^4 + \left(\frac{1}{4}\right)^4 + \text{etc.} \\ & + \left(\frac{1}{2}\right)^4 + \left(\frac{1}{3}\right)^4 + \left(\frac{1}{4}\right)^4 + \text{etc.} \\ & + \left(\frac{1}{3}\right)^4 + \left(\frac{1}{4}\right)^4 + \text{etc.} \\ & + \left(\frac{1}{4}\right)^4 + \text{etc.} \\ & + \text{etc.} \end{aligned}$$

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\* The usual expression for this thickness,  $l = \frac{2S}{JlD}$ , entirely disregards the fact that the liquid is only partly volatilized when reduced to a thin film. For the results of another method of calculating the molecular diameter, see Rühlmann, Volume II., page 237.

The first series is evidently equal to

$$1 + \left(\frac{1}{2}\right)^3 + \left(\frac{1}{3}\right)^3 + \left(\frac{1}{4}\right)^3 + \text{etc.} = \frac{\pi^2}{6}$$

the second is equal to

$$1 + \left(\frac{1}{2}\right)^3 + \left(\frac{1}{3}\right)^3 + \left(\frac{1}{4}\right)^3 + \text{etc.}$$

which is equal to 1.201 + ; so that we have

$$P'' = \frac{3.15}{l} S \quad \text{III.}$$

which, combined with II., gives by an independent method of reasoning the same result as before, namely,

$$JLD = KP'',$$

since we have disregarded signs, and have considered the external pressure equal to zero.

Now the thickness of a molecular film, having been determined by various methods for a few elementary substances, can be calculated for any substance whose graphical symbol is known;\* and hence if the surface tension is given, formula III. enables us to determine the cohesive pressure, and indirectly any of the other physical constants in terms of which it may be expressed.

§ 12. The difference between the specific heats of a substance in the liquid and in the gaseous state is, as we have seen, *other things being equal*, the measure of the work done in separating the particles by the amount corresponding to an increase of one degree in temperature. The sum of all such elementary quantities of work done in an indefinite expansion is the internal latent heat of vaporization; and, conversely, we may regard the difference of these two specific heats as the change of the internal latent heat per degree of temperature, or, what is the same thing, the derivative of this latent heat with respect to the temperature.

In order, however, that this rule may apply in all strictness, the temperature of the liquid and vapor whose specific

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\* See also Rühlmann, *ibid.* "Untersuchungen über die absoluten Grössen der Molecüle."

heats are compared must be the same; and of course the specific heats must be corrected for the external work done in each case. For liquids this may generally be disregarded; but for vapors we must multiply the external pressure in dynes by the coefficient of expansion, remembering to divide by 42,000,000 and by the density, if the result is to be expressed in heat units per unit weight. Deducting this number from the ordinary specific heat, we have that under constant volume. The specific heat of the liquid at the same temperature necessarily exceeds this by the amount of the diminution of the latent heat of vaporization per unit of temperature.

To find an expression for this difference, we have merely to differentiate the equation for the latent heat already found, namely,

$$JLD = \frac{K}{3} Dv_0^2 \frac{m_1}{m} \frac{T}{T_0} \frac{l}{l-l'},$$

where we notice that  $D$  may be cancelled, and that  $K$  is the principal ratio, not far from unity, which we have already calculated for several liquids.

In the liquid or solid state, it must be supposed that the expansion is accompanied by a grouping of the atoms; hence  $K$  must not be disregarded, and we have

$$\begin{aligned} J \frac{dL}{dT} &= \frac{K}{3} \frac{v_0^2}{T_0} \frac{m_1}{m} \left( \frac{(l-l') - l}{(l-l')^2} T \frac{dl}{dT} + \frac{l}{l-l'} \right) \\ &= \frac{K}{3} \frac{v_0^2}{T_0} \frac{m_1}{m} \frac{l}{(l-l')} - \frac{K}{3} \frac{v_0^2 m_1 T}{m T_0} \frac{l'}{(l-l')^2} \frac{dl}{dT} \end{aligned}$$

$= J(H' - H)$ , where  $H$  and  $H'$  are the specific heats of the liquid and of the vapor.

Substituting for  $\frac{dl}{dT}$  its value  $\frac{\epsilon l}{3}$ , we have

$$J(H-H') = \frac{K}{9} v_0^2 \frac{m_1}{m} \frac{T\epsilon}{T_0} \frac{l'l}{(l-l')^2} - \frac{K}{3} \frac{v_0^2}{T_0} \frac{m_1}{m} \frac{l}{(l-l')} I.$$

a formula by which we may determine the difference of specific heats if we know the coefficient of expansion, the factor  $K$  and the ratio of  $l'$  to  $L$ .

The formula may also be written, substituting  $L$  for its value,

$$(H - H') = L \left( \frac{\epsilon l'}{3(l - l')} - \frac{1}{T} \right), \quad \text{I. } a.$$

still involving the ratio of the molecular diameter to the free path.

But since the work done in expansion is the product of the coefficient by the pressure overcome, less the affinity satisfied, we may also write

$$J(H - H') = KP''\epsilon, \quad \text{II.}$$

in which, substituting any value of  $P''$ , we have from III. § 11, from II. § 1, and from III. § 1,

$$J(H - H') D = K \frac{3.15}{l} \frac{S\epsilon}{l} = JLD\epsilon = KE\epsilon^2 T, \quad \text{III.}$$

whence we see that  $(H - H') = L\epsilon$ . IV.

By means of these formulae the difference may be determined between the specific heat in the liquid state and that under constant volume in the state of vapor.

§ 13. We have now considered the principal physical constants, and we find, with the exception of a few relations between them which are independent, that all involve in some way the ratio of the molecular diameter to the free path. It does not, therefore, seem surprising that the relations which still remain to be established should have escaped the notice of a scientific world which has until recently\* been bent upon the solution of the molecular theory of liquids and solids on the false supposition that the molecules were very far apart, and the repulsive

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\* See Rühlmann, *ibid.*

forces exerted at considerable distances, the atoms being hypothetically soft though perfectly elastic bodies.

In the next section we shall consider the ratio of the molecular diameter, or shortening of the free path, to the whole molecular distance; the object of the present section is to obtain formulae for actual use, from which this troublesome factor may have been eliminated.

We have already obtained three equations independent of the free path, namely,

$$\frac{JLD}{E\epsilon T} = K, \quad (1)$$

$$\frac{JLDl}{3.15S} = K, \quad (2)$$

$$L\epsilon = H - H'. \quad (3)$$

We have, moreover, equations involving the ratio of  $l'$  to  $l$ , namely,

$$E\epsilon = \frac{D}{3} \cdot \frac{v_o^2}{T_o} \cdot \frac{m_1}{m} \cdot \frac{l}{l - l'}, \quad (4)$$

$$\epsilon = \frac{3}{T} \cdot \frac{l - l'}{4l' - 3l}, \quad (5)$$

and

$$\left(\frac{l'}{l}\right)^3 \left(1 - \frac{l'}{l}\right) = .11876 \frac{T}{T_1} \frac{(P' + \bar{P})}{P'}. \quad (6)$$

In these equations  $J$ ,  $T_o$ ,  $v_o^2$  and  $\frac{m_1}{m}$  are well-known physical constants.

$$J = 42,000,000 \text{ (C. G. S.)}$$

$$v_o^2 = 33,948,000,000 \text{ (C. G. S.)}$$

$$T_o = 273^\circ \text{ (Centigrade).}$$

$$\frac{m}{m_1} \text{ is half the "molecular weight."}$$



$K$  is the "principal ratio" defined above, which may be calculated approximately for a homogeneous substance by the formula,

$$K = 1 - \frac{\sum m \mathcal{Q}}{20 \sum m},$$

$\mathcal{Q}$  being the "*quantivalence*" of the atom whose molecular weight is  $m$ .

Finally the thickness of the molecular film,  $l$ , which is closely connected with the absolute weight of the molecule, may be calculated with more or less accuracy by reasoning from its value in a known case to that in an unknown. For this, of course, an approximate knowledge of the atomic grouping is necessary.

It is evident that two more data must be had in order to obtain a complete solution of the problem, and these are evidently the free path and the strength of the attraction of each atom. That is, we must have a description in full of the nature and distribution of the material with which we have to deal, in order to be able to predict its specific properties under any imposed conditions.

The determination of the density is evidently equivalent to that of the free path, for, under given conditions of pressure, volume and temperature, the free path is determined, by the kinetic theory, when the density and molecular weight are given; but we are yet unable to determine the attractive power of the various elementary atoms, owing to the insufficiency of the data. It is evident, therefore, *à priori*, that the absolute calculation of the physical constants will be impossible, until by sure but laborious methods these atomic constants shall have been worked out.

We have, therefore, to depend upon six equations to determine the ratios between seven unknown quantities, which is clearly possible. These seven quantities are

the free path, latent heat, elasticity, expansion, critical temperature, specific heat, and capillarity; and it is evident that we may completely eliminate the free path, and have five equations connecting the remaining constants, or, if we choose to leave out the surface tension, which alone involves the doubtful factor  $l$ , have left four equations connecting the five most important physical constants. It follows that, if the value of a single one of these is given, that of all the rest will be determined; if two are given, then the others may be determined, independent either of the molecular distance or of the principal ratio; if three are given, all may be determined, independent of any theoretical consideration.

It is not proposed to work out a multitude of equations which can evidently arise from the various combinations of these quantities; it will be sufficient to deduce a few which will be found convenient for actual use, and others by which the Theory may be thoroughly tested.

For instance, from (1), (4) and (5),

$$Lm\epsilon = (5.922 + 7.896\epsilon T) \left[ 1 - \frac{\Sigma m \mathcal{Q}}{20\Sigma m} \right] \quad \text{I.}$$

From (1) we have

$$LJD = E\epsilon T \left[ 1 - \frac{\Sigma m \mathcal{Q}}{20\Sigma m} \right] \quad \text{II.}$$

From II. and (2) we have

$$lLJD = 3.15 S \left[ 1 - \frac{\Sigma m \mathcal{Q}}{20\Sigma m} \right] \quad \text{III.}$$

From II. and III. we have

$$lE\epsilon T = 3.15 S. \quad \text{IV.}$$

From III. and (3),

$$l(H - H') JD = 3.15 S\epsilon \left[ 1 - \frac{\Sigma m \mathcal{Q}}{20\Sigma m} \right] \quad \text{V.}$$

From (3) directly,

$$(H - H') = L\epsilon. \quad \text{VI.}$$

From I. and VI.,

$$(H - H') m = (5.922 + 7.896\epsilon T) \left[ 1 - \frac{\Sigma m \mathcal{Q}}{20 \Sigma m} \right] \quad \text{VII.}$$

From IV. and V.,

$$(H - H') JD = E\epsilon^2 T \left[ 1 - \frac{\Sigma m \mathcal{Q}}{20 \Sigma m} \right] \quad \text{VIII.}$$

From (4) and (5),

$$E \epsilon^2 m T = 82,898,000 (3 + 4\epsilon T) D. \quad \text{IX.}$$

And finally, from (5) and (6),

$$T_1 \epsilon (3 + 3\epsilon T)^3 P' = 0.11876 (3 + 4\epsilon T)^4 (P' + \bar{P}). \quad \text{X.}$$

These formulae nearly all involve  $\epsilon$ , which is one of the most generally, if not most accurately, known of all the physical constants, thanks to the efforts of Kopp and Pierre. When, however, as in the case of water, the coefficient is hidden under some molecular change, the value may easily be eliminated. It should be remembered, however, that any molecular change that affects the expansion will also alter the compressibility, so that we can no longer depend upon the value of  $E$ .

The relations between the other constants will not in general be disturbed.

§ 14. The truth of the ten equations of the last section is easily shown, in the case of most liquids, to hold within reasonable limits. In many cases, if not in most cases, the error committed by using these formulae is not large as compared with the error of actual observation. To examine in detail the application of these equations to the hundred or more substances whose constants have been determined would require an almost endless amount of labor. A brief consideration may not be out of place.

The general truth of the first equation was anticipated in Miller's *Chemical Physics*, where, on page 342, he gives a table of the *Latent heat for equal Volumes*. The cause of the variation of these latent heats, together with that of their approximate agreement, is now explained, being due to the fact that the coefficient of expansion varies through narrow limits for all ordinary liquids.

The average value of the product of the *internal* latent heat by the molecular weight is easily found from Miller's Table to be about 7,700. The average value of the coefficient of voluminal expansion at the boiling point (say 80°) is not far from .0012;\* the product is therefore about 9.2, and the second term is equal to 5.9 + 3.3, or 9.2 about, which sufficiently establishes the general truth of the formula.

The second formula has been already discussed; the third and the two following are of interest as giving the absolute thickness of a molecule.

We have for water in equation III.

$$l = \frac{3.15 \times 81 \times .93}{575 \times 42,000,000 \times 1} = \text{about ten thousand-mil-}$$

lionths of a centimetre, instead of forty-six, according to Rühlmann. Professor Cooke has suggested five thousand-millionths as the most probable number.†

The formulae for the difference of the internal specific heats of the liquid and vapor are easily shown to agree, as nearly as could be expected, with the observations of Regnault, in which these two specific heats are in no case determined for the same range of temperature.

The specific heat of ether vapor is, for instance, 0.48, nearly, from which, deducting 0.03 for external work, we

\* See Tables for expansion, Sharples, pages 68-72.

† In the *New Chemistry*, page 34, fin.

have 0.45 for the specific heat under constant volume, for a range of temperature from  $70^{\circ}$  to  $220^{\circ}$ . Now since the specific heat of ether is 0.53 at  $0^{\circ}$  and 0.55 at  $35^{\circ}$ , we may assume that at  $70^{\circ}$  it would be about 0.57, and at  $140^{\circ}$  about 0.61, the excess being in the neighborhood of 0.14; the latent heat being 82 (Regnault — Zeuner) and the relative coefficient of expansion about .0017, we should have for both sides of equation VI. the number 0.14, so that, as far as these figures show, the relation may be perfectly exact.

The case of bromine is of unusual interest, it being an elementary liquid; in equation VII. we have without any correction  $H - H' = .0574$ , which multiplied by the molecular weight (160) gives 9.2, nearly. The coefficient of relative expansion being about .0013 at the given temperature ( $80^{\circ} +$ ), gives about 3.7 for the second term in the parenthesis; adding we have 9.6, which finally multiplied by the principal ratio (.95) gives 9.2, nearly, for the other side.

There are many other cases of agreement, and indeed it may be said that there is no case in which the truth of the formulae for specific heat can be disproved; nevertheless, the evidence is negative, and all that is claimed for these formulae is to represent approximately the difference between the specific heats of the liquid and vapor.

When it comes to solid bodies, or such a dense liquid as mercury, a glance will be sufficient to show that these formulae for specific heat do not hold at all; and neither does formula IX. connecting the elasticity and expansion. It would appear as if the cohesive force varied inversely as some power of the distance much less than the fourth, as would be the case if the molecules were in absolute contact during even a considerable portion of the time which we suppose to be occupied by a vibration. By referring to the original formulae, it will be seen that the rate of expansion will be greatly diminished in this case; and hence the constants will nearly all be affected.

The laws for dense solids could easily be established by the same methods of reasoning; but their discussion would exceed the intended limit of this paper. It may, however, be observed that the products of the coefficients are usually from one-third to one-half as great for solids as for liquids, and that the law of variation of the force which binds them together, being compounded probably of attractive and repulsive forces, appears to vary inversely as some power of the distance not far from the square.

The critical temperatures calculated by formula X. come out, for the four liquids examined by Cagniard de la Tour, about ten per cent. higher than his estimate; it is possible that under different conditions a more elevated temperature might have been required, but it is more likely that the theory is at fault. Many considerations have been left out of account which would indicate just such an error. In particular I would mention the same causes which led us before to expect a still greater divergence in the expressions for the pressure at this temperature (§ 10) and the difference between the mean and probable velocity of the molecule, all of which considerations must at present be passed over.

The ten equations of the last article appear to be borne out by experience in the case of a hundred liquids, as closely as one would have a right to expect, in view of the minor considerations which have been of necessity disregarded. By means of a more general analysis, outlined in § 16, I have been able to prove that the same would not have been true if we had assigned an essentially different law to the variation of the cohesive force; the relations calculated between all these constants would have been in that case entirely out of proportion.

§ 15. To facilitate the use and application of the formulae of § 13, connecting the latent heat, elasticity, expan-

sion, specific heat, critical temperature and surface tension, tables have been constructed expressing the value of each of these constants in terms of the ratio of  $l'$  to  $l_0$ , called the *Principal Argument*. In the case of the coefficient of expansion, the ratio was calculated in Table X. explicitly in terms of  $\epsilon$ , for  $0^\circ$  centigrade, by means of the formula I. *a*, of § 7,

$$\text{which became } \frac{l'}{l_0} = \frac{3 + 819 \epsilon}{3 + 1092 \epsilon} \quad \text{I.}$$

For the critical temperature ( $T_1$ ) in Table XI. formula (6) of § 13 was employed, at the temperature zero, neglecting the external pressure. This became

$$T_1 = 32.42 \div \left(\frac{l'}{l_0}\right)^3 \left(1 - \frac{l'}{l_0}\right) \quad \text{II.}$$

For the elasticity at  $0^\circ$  centigrade in Table XII. the equation,

$$\frac{mE_0}{D_0} = \frac{4 \frac{l'}{l_0} - 3}{\left(1 - \frac{l'}{l_0}\right)^2} \times 7.544 \times 10^9 \quad \text{III.}$$

was employed, being obtained by dividing equation (4) of § 13 by equation (5) of the same section, and substituting the values of the constants.

For the latent heat, in Table XIII., calculated at intervals of  $10^\circ$  from  $0^\circ$  to  $150^\circ$ , the fundamental equation I. of § 3 was used in the form,

$$\frac{Lm}{K} = 1.974 T \div \left(1 - \frac{l'}{l}\right) \quad \text{IV.}$$

Finally the difference of the specific heats in the liquid state under constant pressure and under constant volume is calculated in Table XIV. for the same intervals, by a

formula derived from the fundamental equation and from equations (3) and (5) of § 13, namely,

$$\frac{(H-H')m}{K} = 5.922 \div \left(4 \frac{l'}{l} - 3\right) \quad \text{V.}$$

For curiosity's sake, Table XV. was also constructed to show the surface tension at intervals of  $10^\circ$  corresponding to a given ratio of  $l'$  to  $l$ . It was assumed that the density varied as the quotient of the absolute molecular weight by the cube of the absolute molecular distance; and having determined the value of  $l$  for water (about .000,000,01), we have from § 13, IV. and (4), approximately,

$$S \sqrt[3]{\frac{m^2}{D^2}} = 30 \div \left(1 - \frac{l'}{l}\right) \frac{T}{T_0} \quad \text{VI.}$$

by which the value of  $S$  may be calculated roughly from that of  $l' \div l$ , and conversely.

In the construction of the last three tables it was necessary to calculate the ratio,  $l' \div l$ , at various temperatures, in terms of its value at  $0^\circ$ , which might have been done indirectly by means of Table X. and Table III. — the ratio varying inversely as the cube root of the volume. To facilitate this calculation, however, an *auxiliary table* was constructed (XVI.), by means of which, if the ratio of  $l'$  to  $l$  is known at any one temperature, it may be found at any other.

It is easy by means of these tables to find the values of all of the six specific constants of this section, when *any one* is given. By reference to the proper table, the ratio of  $l'$  to  $l_0$  can be found, already reduced to the temperature zero; then with this as an argument, the values of the other constants can be derived, each from its own table. It is assumed that the density and molecular



weight are known, and also the quantivalence of the various atoms which compose the molecule.

To present the results of the theory in the clearest form, and in the smallest possible compass to compare them with those of observation, Table XVIII. has been constructed; the old-fashioned names of the substances, which are exclusively liquids, are placed in the first column; the most modern symbols follow, and to still further identify the liquids, the density, boiling point and melting point are added, mostly from the determinations of Kopp and Pierre. The value of the Principal Argument,  $l' \div l$ , is then tabulated in three columns, calculated respectively from the expansion, the critical temperature and the latent heat.\* The last column contains references to the tables or sections where the liquid in question has received a special examination, so that the comparison may easily be made.

The truth of the theory is illustrated by the general agreement of the values of the Principal Argument calculated from different data; its practical use is limited only by the accuracy with which, from the most probable value of the Argument, the various constants may be derived.

§ 16. The treatment of the specific heat of gases, the tension of vapors and the expansion of liquids subject to a change of state involves the use of the theory of probability, which is foreign to the purpose of this paper. It seemed, however, desirable to show that there was nothing in these phenomena necessarily inconsistent with the law which we have assigned to the variation of the force of cohesion.

The similarity between a *velocity* in the kinetic theory and an *accidental error* in the theory of probability is seen from various considerations. Knowing only, in any spe-

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\* Calling unity the value of  $K$ .

cial case, that the velocity or error is positive and finite, we are able, nevertheless, to calculate from various data the average, the mean, and the probable value. The chances are the same for positive as for negative magnitudes, and the principle of the conservation of energy requires that velocities taken at random, like errors, shall be compounded so that the mean square of the resultant may be equal to the sum of the mean squares of the components.

If we possessed absolutely no knowledge of the mechanism by which velocities are determined, our only choice would be to apply the same rules as to accidental errors; and by comparing the different formulæ which have been suggested for the kinetic theory, one might easily become convinced that the substitution of one formula for another is not likely to cause a mistake of more than one place in the decimal point.

The formula for the probability ( $\phi c$ ) of a velocity of a *gas* molecule, for instance, being less than  $c$ , may be deduced from Watson's formula, in his *Kinetic Theory of Gases*, page 5, namely,

$$\phi c = \frac{4h^3}{\sqrt{\pi}} \int_0^c e^{-h^2 c^2} c^2 dc,$$

while Chauvenet's formula for the probability that an error will be less than  $t$  is

$$\phi t = \frac{2}{\sqrt{\pi}} \int_0^t e^{-t^2} dt.$$

The formulæ for solids and liquids have not apparently been worked out, and, in complete ignorance of the mechanism which determines the kinetic energy of a given particle, we can obtain an approximation, only, to the distribution of velocities, by means of the more general theory of probability. For convenience of reference, a table of the probability of errors has been appended, calculated by

Chauvenet, from 0 to 5 times the probable error; and Mr. Haskell has extended this table in logarithms from 5 to 100 times the probable error. It will therefore be an easy matter to calculate, roughly, the chances of all the different velocities which are likely to occur, and to see whether the various phenomena, such as have been described, can be attributed to the inequality of their distribution according to the laws of chance. The results must be accepted with the greatest caution, as indicating the possibility of explaining the phenomena in this way, and not the probability of having found the true solution.

The internal molecular heat has been so successfully treated of late, by the ordinary assumptions of the Kinetic Theory, that there can be little or no question that the subject is properly a branch of this theory, and consequently, being entirely independent of cohesion, cannot conflict with any supposition as to the nature of the latter.

The question of vapor tensions needs a special examination.

Maxwell has pointed out in his *Theory of Heat*, under the "Molecular Theory of Evaporation and Condensation" (page 323), that a liquid in contact with its vapor is in equilibrium when the rate of evaporation of the liquid is equal to the rate of condensation of the vapor, both being determined by the laws of chance.

By assuming that the total energy of a substance varies as the square of a velocity, we may at once obtain expressions for the probability of a particle of water becoming steam and a particle of steam becoming water, taking into account the interchange across any surface which separates them. The theoretical solution will be of the general form,

$$\left(\frac{D'}{D}\right)^n = A^2 \left( \text{prob}^{-1} \text{co-prob} \frac{1}{A} \sqrt{1 + \frac{L}{W}} \right)^2 \times \left( \frac{BKT}{Lm} \right);$$

the demonstration of this formula (which is itself of slight importance) will be omitted on account of its length.  $A$

is the ratio of the probable to the mean velocity, and  $B$  may be taken as 1.974;  $W$  is the total energy contained in the substance; and  $n$  is nearly equal to unity. The formula indicates, in a general way, the variation of vapor tension with the temperature and in different substances. Solved by the ordinary tables of probability, its results may vary widely from the truth (though seldom by more than one decimal place), which is in part owing to the uncertainty of the true value of  $W$ . Were there a table constructed to represent the actual probability of a velocity bearing various ratios to the probable velocity, one might reasonably expect to obtain more accurate results.

The theory of probability throws much light on the subject of the expansion of liquids near their melting point.

In the solid or crystalline state, bodies may occupy more or less space than in a state of fusion, according to circumstances; and we conclude that there must exist certain molecular arrangements which are more compact, and others less compact, than a simple chance distribution.\*

Whenever a particle contains two or more molecules having, as a system, sufficient velocity to overcome their mutual cohesion, the particle may be said to be in a state of fusion; if, on the other hand, their velocity is so slight that the molecules must return to the same relative positions, the particle may be considered to be solid.

The principle of the distribution of velocities asserts that in any substance in which the mean velocity is given, there are always a certain number of molecules which have, for the moment, more than twice that velocity, for instance; that no matter how high the temperature may be raised, through the inequalities of chance, there will always be *some* molecules whose relative velocities are

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\* A homely illustration might be derived from architecture, in which the general structure is less aggregated, and the solid portions more so, than the materials would be if completely disarranged.

insufficient, for the time being, to carry them out of the sphere of their mutual attraction; and that no matter how low the temperature may be, there will always be *some* which are free to move under the influence of external forces.\*

It follows that in liquids, solid particles, in solids, liquid particles must always be present.

What distinguishes a solid from a liquid is not, therefore, according to this theory, the fact that all particles are either solid or liquid; but simply that the rate of solidification or of liquefaction, as the case may be, is in excess; so that a structure once set up is capable, in solids, of maintaining itself, while in liquids it never attains more than indefinitely small dimensions.

The existence, however, of an indefinite number of these indefinitely small solid particles is easily seen to have a marked influence on the volume whenever in the solid state the density is considerably different from that of the liquid.

Conspicuous amongst all liquids in this respect stands water, which expands greatly on solidifying. In all such liquids, the continual formation of solid particles, be it only for an instant, must tend to increase the volume, and the colder the liquid becomes, the greater will be the proportion of solid particles at any instant; so that, other things being equal, the liquid will expand by cooling.

On the other hand, if the solid be denser than the liquid, the rate of expansion with the temperature will be increased by the gradual disappearance of solid particles.

The existence, therefore, of exceptions to the general law of expansion does not militate in any way against the validity of the reasoning by which it was established.

As in the case of vapor tensions, the quantitative application of the theory of probability is beset with mathe-

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\* The practical effect is seen, undoubtedly, in the slow yielding of the hardest rocks to enormous pressures, discussed in Geology, and in the so-called viscosity of ice.

mathematical difficulty and practical objections. It may perhaps be allowable to suggest that, from almost any point of view, there will be in melting ice only from fifty to seventy per cent. of solid particles, and in freezing water nearly one-half as many, but in boiling water not more than one-third; so that the number which disappear in melting is not more than twice the number which are eliminated when the liquid is raised to boiling. The true expansion, therefore, from  $0^{\circ}$  to  $100^{\circ}$ , instead of being 1.04, may be from 1.08 to 1.10, and the real coefficient at  $0^{\circ}$  is probably from .0006 to .0008, increasing regularly with the temperature, as in the case of an ordinary liquid.

§ 17. The investigation of the hypothesis that the cohesive forces vary inversely as the 4<sup>th</sup> power of the distance has now been carried as far as was originally intended. The results of other hypotheses remain to be determined.

In equation IV. § 2,

$$\mathcal{J}LD = \frac{3}{\alpha - 1} (\bar{P} + E\epsilon T),$$

If a different value be assigned to  $\alpha$ , we can see that the relation between the latent heat and the other constants will be materially altered. There being no reason on the whole to suppose that the value already considered is either too great or too small, and since  $\alpha$  determines, in a certain way, the *average* rate of change of the cohesion, it follows that we are not allowed any great width in the nature of our fundamental hypothesis.

It is not so with the cohesion at short distances. In the condition of equilibrium,

$$\bar{P} + P' + \bar{P}'' = 0,$$

if we write  $P'' : P_0'' = l_0^* : l^*$ , we shall obtain equations as before for the elasticity and the expansion, which may be

at once reduced to the forms already obtained by putting  $x = 6$ .\*

We have

$$E = \frac{P'}{3} \left[ \frac{3l - 2l'}{l - l'} + l \log \frac{l_0}{l} \frac{dx}{dl} - x \right] + \frac{\bar{P}}{3} \left[ l \log \frac{l_0}{l} \frac{dx}{dl} - x \right] \quad \text{I.}$$

$$\epsilon = \frac{3 \left[ 1 - \frac{\bar{P}}{3E} (l \log \frac{l_0}{l} \frac{dx}{dl} - x) \right]}{T \left[ \frac{3l - 2l'}{l - l'} + l \log \frac{l_0}{l} \frac{dx}{dl} - x \right]} \quad \text{II.}$$

whence, by substitution, we shall find  $E\epsilon T = P'$ , as before.

Disregarding  $P$  in comparison with  $E$  or  $P'$ , and treating  $x$  as a constant, we have by differentiation,

$$\begin{aligned} \frac{d\epsilon}{dT} &= \frac{\epsilon^2}{3} (x-3) \frac{\left[ \frac{x-2}{x-3} \right]^2 \left[ \frac{3 + (x-3) \frac{\epsilon T}{3 + (x-2) \frac{\epsilon T}{\epsilon T}}}{3 + (x-2) \frac{\epsilon T}{\epsilon T}} \right] - 1}{\left[ \frac{x-2}{x-3} \right] \left[ \frac{3 + (x-3) \frac{\epsilon T}{3 + (x-2) \frac{\epsilon T}{\epsilon T}}}{3 + (x-2) \frac{\epsilon T}{\epsilon T}} \right] - 1} \\ &= \frac{\epsilon^2}{9} (6x - 15 + \epsilon T (x^2 - 5x + 6)) \quad \text{III.} \end{aligned}$$

$$\frac{d^2\epsilon}{dT^2} = \frac{\epsilon^3}{81} \left\{ 2(6x - 15 + T\epsilon(x^2 - 5x + 6))^2 + 9(x^2 - 5x + 6) \right\} \text{IV.}$$

etc.

From equations III. it is easily seen that  $x$  cannot be constant and less than 3, since it is well known that the rate of expansion increases with the temperature.

There is much however to indicate for  $x$  a smaller value than 6; the rate of expansion does not increase quite so rapidly on the whole as our first analysis would indicate, and from the analogy of small magnets we should expect that at short distances the attraction should vary, for compound substances, inversely as some power of the distance be-

\* It will be noticed that the value of  $x$  is here greater by 2 units than in § 2, denoting the rate of variation of the pressure, not the attraction.

tween the fourth and the square; that is, we should expect to find  $6 > \alpha > 4$ .

The effect of diminishing  $\alpha$  will be evidently to increase the elasticity and to diminish the expansion in like proportion, so that the product  $E\epsilon T$  will not be affected, and hence the principal ratio,  $K$ , will remain the same; but the specific heat, which involves the product  $E\epsilon^2 T$ , will be diminished, as we have already seen is the case in solid bodies.

A diminution of  $\alpha$  would, however, increase the calculated value of the critical temperature, which we have seen is already too high, and this alone is sufficient to counterbalance the weight of the argument founded upon expansion.

By giving different values to  $\alpha$ , all possible relations may be represented between  $\epsilon$  and its derivative; by assigning arbitrary values to  $\alpha$  at different temperatures, any law of expansion can be expressed; and if our reasoning has been correct, when the true relations between the derivatives shall have been determined with still greater accuracy than at present, we shall be able to conclude precisely by what law the cohesion actually varies in different states of aggregation, and we may then class under the head of accurate knowledge what has so far been only hypothetical.

§ 18. The above sections were already in the press when the communication of D. Mendelejeff, *On the Expansion of Liquids*, published in the April Journal of the Chemical Society at London, first came to my notice. The table for the expansion of liquids, quoted from Thorpe, has been reprinted in full (Table VIII.) and is a most striking confirmation of the uniformity of the law of expansion of liquids, pointed out in § 9. One can hardly avoid the conclusion that the experiments of Thorpe must



have been remarkably free from sources of accidental error.

Mendelejeff points out that the law of expansion may be represented, within the limit of error of observation, by the extremely simple empirical formula,

$$V_t = \frac{1}{1 - kt},$$

where  $k$  is a constant very nearly equal to the coefficient of expansion.

By calculating  $k$  for the next to the highest temperature in the table, I find an average error of only five ten-thousandths in the use of this formula for the 47 liquids examined by Thorpe. The formula claims, therefore, a careful investigation.

Differentiating and dividing by the volume, we have

$$\epsilon = \frac{dV}{Vdt} = \frac{k}{1 - kt} \quad \text{I.}$$

$$\frac{d\epsilon}{dt} = \frac{k^2}{(1 - kt)^2} = \epsilon^2 \quad \text{II.}$$

$$\frac{d^2\epsilon}{dt^2} = 2\epsilon^3 \quad \text{III.}$$

$$\frac{d^n\epsilon}{dt^n} = n! \epsilon^n, \text{ etc.}$$

The first derivative is therefore only about one-third as great as the Theory would indicate, and the other derivatives are also much smaller, so that the isobaric curves will be straighter; but from Table VII. it will be sufficiently evident that the whole difference in question is less than the mean difference between two observers such as Kopp and Pierre.

From a purely empirical point of view, it is not easy to decide between the relative values of the formula of Mendelejeff and that of the Theory.

In the case of the 47 liquids examined by Thorpe, it must be frankly admitted that although the observed values lie, in every case but one, between those calculated by the two formulae, the average is twice as near the indication of Mendelejeff as to that of the Theory. More significance would, however, be attached to this fact, were there a sufficient number of observations, made independently, with which the results of Thorpe might be compared. The curvature of the line representing the expansion is subject to a constant error due to the standards of comparison; and the fact that nearly every other observer has found a greater curvature, not only for liquids in general, but also for those few examined in common with Thorpe, should not be left out of account.

For the purpose of comparison, Table IX. was constructed, showing the differences between the volumes according to Mendelejeff's formula and those from the mean results of Kopp and Pierre, for the eleven liquids already examined.

It will be noticed that the volumes for ether do not agree with those calculated by Mendelejeff, owing probably to the use of other data by the same observers, which I have not been able to discover. The figures taken from Sharples' Tables are not so favorable as those quoted in the paper. The sums of the squares of the differences are represented in the table below.

If, for various reasons, butyric acid be omitted from the list, the sums of the squares of the errors will be 2,432,832 for Kopp and Pierre, 2,289,662 for Mendelejeff, and 414,460, for the Theory; or, throwing out fusel-oil, which is most unfavorable to Mendelejeff, the sums will become 1,551,256, 736,953, and 243,518, respectively.

The statement of Mendelejeff, that the empirical formula represents the expansion within the limit of error of observation, is therefore completely borne out in the case

Name of the Liquid.	No. of Temperatures compared.	Sum of the squares of the differences between Kopp and Pierre. (See Table VII.)	Do. between Mendelejeff's formula and their mean. (See Table IX.)	Do. between the Theory and their mean. (See Table VII.)
1. Wood Spirit.	6	358,654	6,379	8,947
2. Alcohol.	7	22,416	24,150	2,986
3. Ether.	3	2,390	2,837	221
4. Aldehyde.	2	114,225	3,249	569
5. Acetate of Ethyl.	7	226,751	90,236	2,180
6. Acetate of Methyl.	5	32,854	16,783	598
7. Formate of Ethyl.	5	13,181	7,722	5,455
8. Fusel-oil.	14	881,576	1,552,709	170,942
9. Butyrate of Methyl.	10	374,221	142,927	145,801
10. Butyrate of Ethyl.	11	406,564	442,670	76,761
11. Butyric Acid.	15	377,433	78,600	1,242,141
Total	85	2,810,265	2,368,262	1,656,601

of these eleven liquids, whether we reject certain of them or not; it is equally obvious that our own formula here affords a still closer approximation. In the case of the seventy-five liquids of Table VII., it will be found that the average ratio between the coefficients, *A*, *B* and *C*, corresponds a little more closely to the Theory than to the empirical formula, being nearly midway between the two.

There are not sufficient data to prove that either formula may not be absolutely true; but the indication of such

facts as we possess is that the truth must lie between them.

It was pointed out in § 10 that, in expansion, the free path would increase with the distance *more* than one might expect, by an amount which could be calculated, for instance, in the case of spherical atoms.

The impact, which is necessarily central in the most condensed state, would often be oblique in a state less condensed. The effect of thus increasing the length of the free path would be to diminish the visible expansion and also its rate of change. The same is true of the rapidly increasing vapor tension, and these considerations, together with those given in the last section, are sufficient to account for a much greater difference than actually exists between the theoretical and empirical formulae.

The latter is undoubtedly, as Mendeleeff claims, a *first approximation* to the expression of the facts; the former, to their exact theoretical solution. The close agreement of the formulae must be considered as a mutual confirmation.

§ 19. In the same April Journal of the Chemical Society will be found an article by Thorpe and Rücker *On a Relation between the Critical Temperatures of Bodies and their Thermal Expansions as Liquids*.

The formula of Van der Waals is first considered, namely, that *at corresponding temperatures*,

$$\frac{1}{V_i} \frac{dV_i}{dt} \times T_i = C, \quad \text{I.}$$

in which the first factor is evidently the same as our  $\epsilon$ . This formula, by the way, may be derived from § 13.

In (6) we have

$$\left(\frac{l'}{l}\right)^3 \left(1 - \frac{l'}{l}\right) = .11875 \frac{T}{T_i} \frac{(P' + \bar{P})}{P'}$$

where, neglecting the last factor, which is nearly equal to 1, we see that if we know the ratio of  $T_i$  to  $T$ , which is

the same, by definition, for all liquids at *corresponding temperatures*, the ratio of  $l'$  to  $l$  must be determined. We have, therefore, for the coefficient of expansion, from (5),

$$\epsilon = \frac{3}{T} \frac{1 - \frac{l'}{l}}{4 \frac{l'}{l} - 3},$$

where we see that if  $\frac{l'}{l}$  is given,  $\epsilon$  varies inversely as the temperature.

Therefore  $\epsilon : \epsilon' = T' : T = T'_1 : T_1$ , or  $\epsilon T_1 = \text{constant}$ .

By combining this result with Mendelejeff's formula for expansion,

$$V_t = \frac{1}{1 - kt},$$

Thorpe and Rücker obtain the following:

$$\frac{V_0}{V_t} = \frac{aT_1 - T}{aT_1 - 273}, \quad \text{II.}$$

whence

$$a = \frac{TV_t - 273}{T_1(V_t - 1)} \quad \text{III.}$$

The mean value of  $a$  is calculated for 7 liquids, the critical temperature being determined by Sajotschewsky, as 1.995; from 5 other determinations, 1.976; from 10 by Pawlewski, 1.991; and from 12 others, 1.93. Selecting the most probable value, 1.995, the critical temperatures of the first 7 liquids are calculated by the formula,

$$T_1 = \frac{TV_t - 273}{1.995(V_t - 1)}, \quad \text{IV.}$$

with a remarkable degree of approximation, the average error being very little more than one degree, which is of

course very much smaller than the probable error of observation.

Table XVII. has been constructed to show the probable error when *all* the liquids quoted are taken into account, and to compare this error with that of the Theory. It will be seen that the average error is here in the tens and not in the units, and that the probable error of the Theory is a little smaller, and could be made very much so, had it been thought advisable to introduce the empirical constant, 0.116, instead of that calculated from purely theoretical considerations (.11876).

The use of either formula is of practical importance, and the difference between their indications is no greater than the limit of error of observation. This is owing to the close agreement, at low temperatures, of the formulae for expansion (already considered), by which, in combination with the principle of Van der Waals, the critical temperature might be calculated in each case.

Both formulae agree in indicating, for all liquids, an invariable ratio between the densities at the absolute zero and at the critical temperature. From the empirical formula (II.), we see that this ratio should be  $a \div (a - 1)$ , or 2.005, nearly, while the Theory requires the cube of  $l_c \div l'_c$  or about 3.4. Various considerations, whose discussion would be unprofitable, tend to diminish this theoretical value; but a single accurate determination of the density of a liquid in the critical state would probably serve as a crucial test of the reasoning.

§ 20. Conclusion:—(1) It is not claimed that the theory which has been developed is by any means a complete solution of the relations existing between the various constants of Thermodynamics; the main point has been to show that such relations exist. The provisional assumption of a cohesive force varying inversely as the fourth

power of the distance may be considered as the first link in the chain by which these may finally be connected together.

(2) The connection between these constants is exemplified in a series of six tables, in which they are all expressed, explicitly or implicitly, in terms of certain well-known constants, and one which is peculiar to this theory, called the Principal Argument. It has not been attempted to adjust these tables empirically (which might easily have been done) so as to obtain the best possible results; they represent rigidly the relation between the six physical constants required by the Theory for an ideal liquid or solid.

(3) The indications of this theory are in many cases within the limits of errors of observation, and in no case are we led to a result which is not reasonably close to the truth, considering the quantities which have been neglected. The same would not have been true if any fundamental change had been made in the supposition as to the nature of the cohesive force or its rate of variation, the general law for which may, therefore, be considered as established.

(4) In view of the magnitudes of several of the quantities treated, the approximate agreement of the results precludes any essential error in the formulae.

(5) In working out the mathematical solution of various problems, we had frequent recourse to certain formulae which were already developed in Maxwell's *Electricity and Magnetism*. We have followed, all through, the analogy between the attraction of a number of small magnetized spheres and the ordinary phenomena of cohesion. The analogy appears to hold in every respect. On the other hand, the laws of the attraction assigned to ordinary unpolarized matter have been proved to be entirely incompatible with the known facts.

(6) There being nothing inconsistent with any of the phenomena known to Chemistry or Physics in the supposition that the ultimate particles of matter, of whatsoever sort, have fundamentally the same characteristics, may it not be that the same causes which, under certain conditions, render the particles of steel and other substances permanently magnetic, belong in reality to the elementary atoms of which all bodies are composed, like the polarities assigned to them in electrolysis, whether the body as a whole exhibits magnetic or diamagnetic properties? If this should be so, then we have found the physical basis for a Theory of Cohesion.



## TABLES.

# Table of the Probability of Errors. (Probable Error = 1.)

*Derived from Chauvenet's Astronomy, Vol. II, Table IX, A*

Error less than	Probability.	Difference for 0.01	Error greater than	Probability.	Difference for 0.01
0.0	0.00000	.00538	2.5	0.09175	.00129
0.1	0.05378	.00537	2.6	0.07949	.00115
0.2	0.10731	.00533	2.7	0.06859	.00102
0.3	0.16035	.00527	2.8	0.05895	.00090
0.4	0.21268	.00519	2.9	0.05046	.00079
0.5	0.26407	.00509	3.0	0.04302	.00069
0.6	0.31430	.00496	3.1	0.03654	.00060
0.7	0.36317	.00481	3.2	0.03090	.00052
0.8	0.41052	.00465	3.3	0.02603	.00045
0.9	0.45618	.00448	3.4	0.02183	.00038
1.0	0.50000	.00429	3.5	0.01824	.00033
1.1	0.54188	.00407	3.6	0.01518	.00028
1.2	0.58171	.00388	3.7	0.01257	.00024
1.3	0.61942	.00367	3.8	0.01038	.00020
1.4	0.65498	.00345	3.9	0.00853	.00017
1.5	0.68833	.00324	4.0	0.00698	.00014
1.6	0.71949	.00301	4.1	0.00569	.00012
1.7	0.74847	.00279	4.2	0.00461	.00009
1.8	0.77528	.00258	4.3	0.00373	.00008
1.9	0.79999	.00237	4.4	0.00300	.00007
2.0	0.82266	.00217	4.5	0.00240	.00005
2.1	0.84335	.00197	4.6	0.00192	.00004
2.2	0.86216	.00179	4.7	0.00152	.00003
2.3	0.87918	.00162	4.8	0.00121	.00003
2.4	0.89450	.00146	4.9	0.00095	.00002
2.5	0.90825	.00130	5.0	0.00074	.00002

# Table of the Logarithmic Probability of Errors.

Probable Error = 1. (Haskell.)

Error greater than	Logarithm of Probability.	Difference.	and Difference.	Error greater than	Logarithm of Probability.	Difference.	and Difference.
5.0	<u>4.8722</u>	.2165	74	Logarithmic probability continued, accurate to four figures.			
5.2	<u>4.6557</u>	.2239	75	10	<u>11.185</u>	2.115	194.
5.4	<u>4.4318</u>	.2314	75	11	<u>13.070</u>	2.309	195
5.6	<u>4.2004</u>	.2389	75	12	<u>16.762</u>	2.504	195
5.8	<u>5.9615</u>	.2464	76	13	<u>18.258</u>	2.699	195
6.0	<u>5.7151</u>	.2540	75	14	<u>21.559</u>	2.894	196
6.2	<u>5.4611</u>	.2615	76	15	<u>24.665</u>	3.090	196
6.4	<u>5.1996</u>	.2691	76	16	<u>27.575</u>	3.286	196
6.6	<u>6.9305</u>	.2767	76	17	<u>30.289</u>	3.482	196
6.8	<u>6.6538</u>	.2843	76	18	<u>34.807</u>	3.678	197
7.0	<u>6.3695</u>	.2919	77	19	<u>37.129</u>	3.865	
7.2	<u>6.0776</u>	.2995	77	20	<u>41.254</u>		
7.4	<u>7.7781</u>	.3072	76	Logarithmic probability continued, containing four significant figures.			
7.6	<u>7.4709</u>	.3148	78	10	<u>11.18</u>	29.93	19.64
7.8	<u>7.1561</u>	.3226	76	20	<u>41.25</u>	49.57	19.70
8.0	<u>8.8335</u>	.3302	77	30	<u>91.68</u>	69.27	19.74
8.2	<u>8.5033</u>	.3379	76	40	<u>160.41</u>	89.01	19.74
8.4	<u>8.1654</u>	.3455	77	50	<u>249.40</u>	108.75	19.74
8.6	<u>9.8199</u>	.3532	77	60	<u>358.65</u>	128.49	19.76
8.8	<u>9.4665</u>	.3609	77	70	<u>486.16</u>	148.25	19.74
9.0	<u>9.1056</u>	.3686	78	80	<u>635.91</u>	167.99	19.76
9.2	<u>10.7370</u>	.3764	78	90	<u>803.92</u>	187.75	
9.4	<u>10.3606</u>	.3842	77	100	<u>990.17</u>		
9.6	<u>11.9764</u>	.3919	77				
9.8	<u>11.5845</u>	.3996	78				
10.0	<u>11.1849</u>						

# I.

## Table for Epsilon and its Derivatives.

*Containing four significant figures calculated for*

$$T = 273^{\circ}$$

$\epsilon$	$D_{T\epsilon}$ .0000	$D_{T^2\epsilon}$ .000000	$D_{T^3\epsilon}$ .00000000	$D_{T^4\epsilon}$ .0000000000
.0001	0002369	00001264	000001068	0000001239
.0002	0009624	00010470	000018040	0000042700
.0003	0021980	00036540	000096300	0000349000
.0004	0039660	00089500	000320400	0001581000
.0005	0062880	00180500	000824200	0005180000
.0006	0091860	00322100	001797000	0013820000
.0007	0126800	00527900	003501000	0032000000
.0008	0167900	00812600	006273000	0066760000
.0009	0215500	01193000	010550000	0142600000
.0010	0269700	01687000	016850000	0232500000
.0011	0330900	02313000	025870000	0399500000
.0012	0398900	03091000	038370000	0658000000
.0013	0474400	04046000	054630000	1045000000
.0014	0557300	05199000	077300000	1611000000
.0015	0647100	06577000	107300000	2417000000
.0016	0746400	08206000	145000000	3544000000
.0017	0853300	10110000	192900000	5093000000
.0018	0968300	12340000	253000000	7185000000
.0019	1092000	14900000	327600000	9972000000
.0020	1225000	17610000	419200000	13643000000

## II.

### Table of Coefficients of Volume.

*Containing four significant figures.*

$$V = 1 + at + bt^2 + ct^3 + dt^4 + et^5 + \&c.$$

<i>a</i> .00	<i>b</i> .00000	<i>c</i> .0000000	<i>d</i> .000000000	<i>e</i> .00000000000
01	001684	00003458	0000007892	00000001498
02	006812	00028400	0000131900	00000051100
03	015490	00098370	0000697200	00000413300
04	027830	00239100	0002299000	00001854000
05	043940	00478800	0005851000	00006020000
06	063930	00848400	0012640000	00015930000
07	087900	01381000	0024410000	00036560000
08	115900	02111000	0043350000	00075630000
09	148200	03079000	0072290000	00156000000
10	184800	04327000	0115000000	00263800000
11	225900	05897000	0174500000	00442600000
12	271400	07833000	0256900000	00724000000
13	321700	10190000	0364500000	01142000000
14	376600	13020000	0511100000	01748000000
15	436000	16370000	0702300000	02608000000
16	501200	20320000	0943100000	03801000000
17	571100	24910000	1246000000	05435000000
18	646100	30250000	1621000000	07626000000
19	726500	36340000	2089000000	10530000000
20	812500	42930000	2651000000	14300000000

# III. TABLE OF VOLUMES.

*Significant to four decimal places besides the zeros preceding.*

VOLUME AT  $0^{\circ} = 1.000000$ .

$\epsilon$	$-10^{\circ}$	$10^{\circ}$	$20^{\circ}$	$30^{\circ}$	$40^{\circ}$	$50^{\circ}$	$60^{\circ}$	$70^{\circ}$
.0001	0.999002	1.001002	1.002007	1.003015	1.004027	1.005042	1.006062	1.007084
.0002	0.998007	1.002007	1.004027	1.006062	1.008109	1.010170	1.012260	1.014340
.0003	0.997015	1.003015	1.006063	1.009142	1.012260	1.015400	1.018580	1.021790
.0004	0.996028	1.004028	1.008113	1.012260	1.016470	1.020730	1.025070	1.029450
.0005	0.995044	1.005044	1.010180	1.015410	1.020730	1.026160	1.031690	1.037320
.0006	0.994063	1.006065	1.012270	1.018600	1.025070	1.031720	1.038500	1.045450
.0007	0.993087	1.007089	1.014360	1.021830	1.029510	1.037400	1.045490	1.053850
.0008	0.992114	1.008118	1.016480	1.025100	1.034000	1.043180	1.052700	1.062510
.0009	0.991145	1.009151	1.018610	1.028420	1.038590	1.049140	1.060110	1.071520
.0010	0.990180	1.010180	1.020770	1.031790	1.043270	1.055240	1.067750	1.080880
.0011	0.989210	1.011230	1.022950	1.035200	1.048030	1.061510	1.075660	1.090580
.0012	0.988260	1.012280	1.025150	1.038670	1.052920	1.067940	1.083850	1.100700
.0013	0.987310	1.013330	1.027380	1.042210	1.057900	1.074580	1.092340	1.111300
.0014	0.986370	1.014390	1.029620	1.045780	1.063010	1.081410	1.101200	1.123400
.0015	0.985420	1.015460	1.031880	1.049430	1.068240	1.088470	1.110400	1.134100
.0016	0.984480	1.016520	1.034180	1.053150	1.073600	1.095780	1.120000	1.146500
.0017	0.983550	1.017590	1.036500	1.056920	1.079110	1.103300	1.130000	1.159400
.0018	0.982620	1.018680	1.038850	1.060780	1.084770	1.111200	1.140500	1.173300
.0019	0.981690	1.019770	1.041230	1.064720	1.090590	1.119300	1.151500	1.187900
.0020	0.980770	1.020850	1.043630	1.068710	1.096580	1.127800	1.163000	1.203300

# III. TABLE OF VOLUMES (continued).

*Significant to four decimal places besides the zeros preceding.*

VOLUME AT 0° = 1.000000.

°	80°	90°	100°	110°	120°	130°	140°	150°
.0001	1.008110	1.009136	1.010117	1.011120	1.01225	1.01329	1.01433	1.01539
.0002	1.016450	1.018570	1.02068	1.02286	1.02503	1.02721	1.02943	1.03163
.0003	1.025040	1.028320	1.03166	1.03501	1.03841	1.04166	1.04534	1.04886
.0004	1.033910	1.038440	1.04304	1.04772	1.05247	1.05731	1.06222	1.06720
.0005	1.043080	1.048950	1.05494	1.06106	1.06729	1.07367	1.08017	1.08686
.0006	1.052580	1.059890	1.06738	1.07509	1.08297	1.09108	1.09944	1.10800
.0007	1.062450	1.071310	1.08045	1.08990	1.09964	1.10970	1.12020	1.13100
.0008	1.072700	1.083250	1.09421	1.10560	1.11740	1.12970	1.14260	1.15600
.0009	1.083420	1.095810	1.10880	1.12330	1.13650	1.15150	1.16710	1.18370
.0010	1.094610	1.109300	1.12420	1.14030	1.15720	1.17490	1.19390	1.21400
.0011	1.106300	1.123000	1.14060	1.15940	1.17940	1.20080	1.22360	1.24790
.0012	1.118700	1.137800	1.15820	1.18020	1.20370	1.22910	1.25650	1.28600
.0013	1.131700	1.153600	1.17710	1.20260	1.23030	1.26040	1.29320	1.32900
.0014	1.145500	1.170400	1.19750	1.22720	1.25960	1.29540	1.33450	1.37780
.0015	1.160100	1.188300	1.21960	1.25650	1.29220	1.33450	1.38140	1.43370
.0016	1.175600	1.207800	1.24360	1.28350	1.32830	1.37830	1.43460	1.49810
.0017	1.192300	1.228900	1.26990	1.31630	1.36850	1.42800	1.49550	1.57200
.0018	1.210000	1.251400	1.29860	1.35250	1.41390	1.48430	1.56490	1.65750
.0019	1.229200	1.276200	1.33030	1.39810	1.46490	1.55700	1.64490	1.75700
.0020	1.249600	1.302900	1.36490	1.43720	1.52180	1.62040	1.73580	1.87050

TABLE IV.  
Containing four significant figures.

ε	—10°				0°				10°			
	A	B	C	A	B	C	A	B	C	A	B	C
.0001	.0100	.001684	.00003411	.0100	.001684	.00003458	.0100	.001684	.00003458	.0100	.001684	.00003505
.0002	.0200	.006807	.00027620	.0200	.006812	.00028400	.0200	.006807	.00028400	.0200	.006807	.00029200
.0003	.0300	.015480	.00094290	.0300	.015490	.00098370	.0300	.015480	.00098370	.0300	.015480	.00102600
.0004	.0400	.027800	.00225800	.0400	.027830	.00239100	.0400	.027800	.00239100	.0400	.027800	.00253400
.0005	.0500	.043880	.00445200	.0500	.043940	.00478800	.0500	.043880	.00478800	.0500	.043880	.00515400
.0006	.0600	.063800	.00776500	.0600	.063930	.00848400	.0600	.063780	.00848400	.0600	.063780	.00928300
.0007	.0700	.087650	.01244000	.0700	.087900	.01381000	.0700	.087610	.01381000	.0700	.087610	.01536000
.0008	.0800	.115500	.01871000	.0800	.115900	.02111000	.0800	.115500	.02111000	.0800	.115500	.02391000
.0009	.0900	.147500	.02684000	.0900	.148200	.03079000	.0900	.147300	.03079000	.0900	.147300	.03552000
.0010	.1000	.183700	.03703000	.1000	.184800	.04327000	.1000	.183300	.04327000	.1000	.183300	.05083000
.0011	.1100	.224300	.04961000	.1100	.225900	.05897000	.1100	.223700	.05897000	.1100	.223700	.07055000
.0012	.1200	.269000	.06472000	.1200	.271400	.07833000	.1200	.268200	.07833000	.1200	.268200	.09556000
.0013	.1300	.318400	.0829—000	.1300	.321700	.10190000	.1300	.317000	.10190000	.1300	.317000	.12670000
.0014	.1400	.372000	.10390000	.1400	.376600	.13020000	.1400	.370000	.13020000	.1400	.370000	.16530000
.0015	.1500	.429900	.12810000	.1500	.436000	.16370000	.1500	.426700	.16370000	.1500	.426700	.21230000
.0016	.1599	.493100	.15610000	.1600	.501200	.20320000	.1601	.488500	.20320000	.1601	.488500	.26930000
.0017	.1699	.560700	.18790000	.1700	.571100	.24910000	.1701	.554100	.24910000	.1701	.554100	.33750000
.0018	.1799	.632900	.22430000	.1800	.646100	.30250000	.1801	.623700	.30250000	.1801	.623700	.41890000
.0019	.1899	.709800	.26440000	.1900	.726500	.36340000	.1901	.697200	.36340000	.1901	.697200	.51500000
.0020	.1999	.791900	.30590000	.2000	.812500	.42930000	.2003	.774700	.42930000	.2003	.774700	.62410000



TABLE IV. (continued).

Containing four significant figures.

$\epsilon$	20°			30°			40°		
	A	B	C	A	B	C	A	B	C
.0001	.01000	.001684	.00003554	.01000	.001683	.00003603	.01000	.001683	.00003653
.0002	.02000	.006806	.00030030	.02000	.006798	.00030880	.02000	.006787	.00031770
.0003	.03000	.015460	.00107100	.03000	.015410	.00111800	.03000	.015350	.00116800
.0004	.04000	.027720	.00268600	.04000	.027570	.00284700	.04001	.027360	.00301700
.0005	.05000	.043650	.00555000	.05001	.043260	.00597600	.05003	.042680	.00643300
.0006	.06001	.063290	.01016000	.06002	.062420	.01112000	.06006	.061100	.01216000
.0007	.07001	.086650	.01711000	.07005	.084890	.01902000	.07012	.082200	.02113000
.0008	.08002	.113700	.02708000	.08009	.110500	.03062000	.08024	.105500	.03455000
.0009	.09010	.144300	.04102000	.09017	.138500	.04731000	.09042	.129500	.05438000
.0010	.10010	.178400	.05971000	.10030	.169100	.06990000	.10060	.154500	.08143000
.0011	.11010	.216100	.08434000	.11040	.201400	.10030000	.11110	.178200	.11860000
.0012	.12010	.256600	.11640000	.12060	.234300	.14090000	.12170	.198400	.16900000
.0013	.13030	.300200	.15700000	.13090	.267100	.19320000	.13250	.213600	.23510000
.0014	.14030	.345700	.20900000	.14130	.297700	.26150000	.14360	.219500	.32280000
.0015	.15050	.392600	.27410000	.15190	.324200	.34880000	.15510	.212200	.43740000
.0016	.16070	.441500	.35440000	.16260	.346200	.45850000	.16710	.189200	.58160000
.0017	.17090	.490200	.45300000	.17360	.359700	.59570000	.17980	.143100	.76560000
.0018	.18120	.538200	.57330000	.18480	.362000	.76590000	.19320	+0679-0	.99660000
.0019	.19160	.584100	.71930000	.19650	.349100	.97630000	.20770	-0455-0	.128590000
.0020	.20210	.627200	.89040000	.20850	.318400	.122820000	.22340	-203300	.163760000

TABLE IV. (continued.)

Containing four significant figures.

°	50°			60°			70°		
	A .00	B .00000	C .000000	A .00	B .00000	C .000000	A .00	B .000000	C .0000000
.0001	01000	001682	000003704	01000	001681	00003755	01000	01680	00003808
.0002	02000	006772	000032680	02000	006753	00033610	02000	06730	00034570
.0003	03001	015270	000121900	03001	015160	00127200	03001	15020	00132700
.0004	04002	027060	000319700	04003	026680	00338600	04007	26210	00358400
.0005	05005	041880	000692000	05011	040840	00743700	05017	39550	00798300
.0006	06013	059260	001327000	06023	056860	01447000	06040	53840	01574000
.0007	07026	078450	002341000	07049	073490	02589000	07082	67220	02854000
.0008	08050	098450	003886000	08091	0938-0	04354000	08154	770-0	04859000
.0009	09089	116600	006223000	09167	0994-0	07086000	09284	771-0	08026000
.0010	10150	133400	009427000	10270	105100	10840000	10470	685-0	12390000
.0011	11230	144700	013900000	11440	0994-0	16160000	11740	+407-0	18650000
.0012	12350	146500	020070000	12670	0759-0	23600000	13160	-161-0	27490000
.0013	13530	135700	028270000	14000	+0294-0	33590000			
.0014	14770	105000	039210000	15480	-0524-0	47150000			
.0015	16120	+0473-0	053740000						
.0016	17570	-0433-0	072370000						
.0017	19150	-179200	096260000						
.0018	20940	-371700	126500000						
.0019	22940	-637700	164800000						
.0020	25210	-989500	211800000						

# TABLE IV. (concluded).

Containing four significant figures.

$\epsilon$	80°			90°			100°		
	A	B	C	A	B	C	A	B	C
.0001	.00	.000000	.0000000	.00	.000000	.0000000	.00	.000000	.0000000
.0002	01000	01678	00003861	01000	01676	00003914	01000	01674	00003969
.0003	02000	06703	00035550	02001	06672	00036550	02001	06636	00037600
.0004	03003	14870	00138400	03004	14690	00144400	03005	14470	00150500
.0005	04010	25640	00379200	04014	24970	00400700	04021	24190	00423300
.0006	05027	37970	00856000	05040	36100	00916600	05057	33890	00978000
.0007	06062	50140	01710000	06093	45700	01854000	06133	40460	02005000
.0008	07129	59480	03138000	07193	50160	03439000	07278	39110	03760000
.0009	08245	623-0	05403000	08369	443-0	05984000	08532	+229-0	06604000
.0010	09452	494-0	09045000	09684	+156-0	08701000	09996	-249-0	11310000
.0011	10740	+227-0	14070000	11120	-331-0	15880000			
	12190	-330-0	21350000						

**Table V.** — *Calculation of the mean difference between Pierre and Köpp.*

	A	B .00000	C .0000000	$\Delta^2 A$ $10^{-9} \times$	$\Delta^2 B$ $10^{-12} \times$	$\Delta^2 C$ $10^{-16} \times$
1. Wood Spirit.						
P	.001185569	15649300	0911100			
K	.001134200	13635000	0874100			
	2) +.000051369	2) +02014300	2) +0037000	2.639	0.041	0.001
	.000025685	01007150	0018500			
	.001159885	14642150	0892600			
2. Alcohol.						
P	.001048630	17509900	0134518			
K	.001041390	07836000	1761800			
	+ .000007240	+09673900	—1627282	0.052	0.936	2.647
	.000003620	04836950	0813641			
	.001045010	12672950	0948159			
3. Aldehyde.						
P	.001653500	85060000	6425800			
K	.001546400	69745000				
	+ .000107100	+15315000		11.471	2.346	—
	.000053550	07657500				
	.001599950	77402500				
4. Ether.						
P	.001513240	23590000	4005100			
K	.001480260	35031600	2700700			
	+ .000032980	—11441600	+1304400	1.088	1.309	1.700
	.000016490	05720800	0652200			
	.001496750	29310800	3352900			
5. Formate of Ethyl.						
P	.001325200	28624840	0661800			
K	.001364460	01353800	3924800			
	— .000039260	+27271040	—3263000	1.541	7.437	10.647
	.000019630	13635520	1631500			
	.001344830	14989320	2293300			
6. Acetate of Methyl.						
P	.001295950	29098000	0425690			
K	.001277900	39471000	0363900			
	+ .000018050	—10373000	+0061790	0.326	1.076	0.004
	.000009025	05186500	0030895			
	.001286925	34284500	0394795			
7. Acetate of Ethyl.						
P	.001258490	29568800	1492150			
K	.001273800	21914000	1179700			
	— .000015310	+07654400	+0312450	0.234	0.585	0.097
	.000007655	03827200	0156225			
	.001266145	25741200	1335925			

**Table V.** — *Calculation of the mean difference between Pierre and Kopp.*

	A	B	C	$\Delta^2 A$ $10^{-9} \times$	$\Delta^2 B$ $10^{-12} \times$	$\Delta^2 C$ $10^{-16} \times$
8. Butyric Acid.	P * $\int$ .001025700 † $\{$ .001030400 2) .002056100 .001028050 .001046100 — .000018050 .000009025 .001037075	.000000 08376000 08188900 2) 16564900 08282450 05624400 + 02658050 01329025 06953425	.00000000 0346900 0333200 2) 0680100 0340050 0542010 — 0201960 0100980 0441030			
9. Butyrate of Methyl.	P .001239890 K .001195650 + .000044240 .000022120 .001217770	06260240 18103000 — 11842760 05921380 12181620	1306500 0982920 + 0323580 0161790 1144710	0.326  1.957	0.071  1.402	0.041  0.105
10. Butyrate of Ethyl.	P† $\{$ [ .000632742 ] K§ $\{$ .001202790 .001178170 + .000024620 .000012310 .001190480	[ 127630000 ] 00722338 13093000 — 12370662 06185331 06907669	[ 5027800 ] 2263460 0956000 + 1307460 0653739 1609730	0.606	1.530	1.710
11. Fusel-oil.	P ¶ $\{$ .000890100 .000898850 .001788950 .000894475 K .000972400 — .000077925 .000038962 .000933437	06572900 06874460 13447360 06723680 — 08565100 + 15288780 07644390 — 00920710	1184580 1009600 2194180 1097090 2021800 — 0924710 0462355 1559455	6.073	2.338	0.855
	Mean Difference. .0000 489 ---	Mean Difference. .00000 1318 ----	Mean Difference. .0000000 1345 ---	11) 26.313 2.392 √ 23.92 489	11) 19.071 1.734 √ 1.73.40 1318	10) 17.807 1.781 √ 1.78.10 1345
	* 0° to 100° † 100° to 163°. 4	† 99° to 119°. 4 § + 13° to 99°		— 15° to + 80° ¶ 80° to 132°. 1		

# VI. Table of the Value of

No. of Liquid	A			$\Delta A$		B	$\Delta B$		C	$\Delta C$		
	Assumed Observed			Calculated Observed			Calculated Observed					
	.00	.00			.00000					.0000000		
1	0578	0576	2	0418	1347	929	015	—	—			
2	0674	0674	0	0685	1721	1036	022	-005	27			
3	0751	0747	4	0711	1810	1099	037	—	—			
4	0783	0787	4	0741	0513	228	042	027	15			
5	0802	0804	2	0617	1246	626	050	—	—			
6	0804	0805	1	0760	1033	273	047	—	—			
7	0813	0811	2	0455	0640	185	055	014	41			
8	0820	0817	3	0944	0919	25	046	006	17			
9	0824	0825	1	0449	0730	281	057	013	44			
10	0827	0826	1	0770	0522	248	052	014	38			
11	0837	0842	5	0610	0222	388	058	035	23			
12	0838	0844	6	0770	0401	369	055	026	29			
13	0841	0835	6	0955	0675	280	052	013	39			
14	0861	0859	2	0770	0442	328	061	027	34			
15	0888	0888	0	1134	1924	793	058	029	29			
16	0895	0894	1	0771	0853	82	071	026	45			
17	0909	0906	3	1166	3662	2496	062	-250	312			
18	0925	0929	4	1345	3140	1795	060	-049	109			
19	0928	0931	3	0771	-0063	834	080	050	30			
20	0928	0934	6	1000	0307	693	075	058	17			
21	0939	0940	1	1005	-0820	1825	078	081	3			
22	0939	0941	2	1005	0381	624	078	049	29			
23	0941	0936	5	1216	1242	26	072	-032	104			
24	0941	0943	2	1216	1346	130	072	009	63			
25	0951	0953	2	1233	0757	476	075	003	72			
26	0952	0954	2	1538	2214	676	059	564	505			
27	0955	0959	4	1420	1901	481	068	465	397			
28	0962	0959	3	1250	0038	1212	078	073	5			
29	0962	0965	3	1250	1231	19	078	024	54			
30	0965	0962	3	1445	1865	420	071	029	42			
31	0986	0979	7	1495	0967	528	076	018	58			
32	0986	0985	1	1495	0608	887	076	049	27			
33	0994	0994	0	1300	1090	210	088	015	73			
34	0996	0993	3	1520	0625	895	079	060	19			
35	0996	1000	4	1520	1738	218	079	108	29			
36	1011	1009	2	0711	0333	378	083	052	31			
37	1017	1017	0	1569	1576	7	085	019	66			

# A, B and C Calculated and Observed.

No. of Liquid	A		$\Delta A$	B		$\Delta B$	C		$\Delta C$
	Assumed	Observed		Calculated	Observed		Calculated	Observed	
	.00	.00		.00000			.0000000		
38	1027	1032	5	1592	1726	134	089	015	74
39	1032	1032	0	1034	0083	951	124	077	47
40	1041	1038	3	1935	1711	224	070	054	16
41	1047	1053	6	1368	1839	471	099	008	91
42	1048	1047	1	1640	1378	262	096	018	78
43	1048	1057	9	1640	0183	1457	096	096	0
44	1050	1048	2	1040	-0240	1280	119	082	37
45	1069	1071	2	1390	0033	1357	117	074	43
46	1074	1069	5	1028	0842	186	073	047	26
47	1080	1079	1	1402	1555	153	121	—	—
48	1101	1100	1	0142	0218	76	130	070	60
49	1101	1107	6	2161	4665	2504	084	-174	258
50	1114	1119	5	2047	1047	1000	104	103	1
51	1122	1121	1	1802	0170	1632	124	059	65
52	1124	1129	5	2080	4792	2712	108	-184	292
53	1132	1133	1	1822	0912	910	129	076	53
54	1141	1140	1	2323	1371	952	097	191	94
55	1141	1142	1	2323	1964	359	097	062	35
56	1150	1150	0	1451	-0090	1541	151	130	21
57	1171	1175	4	2444	3577	1133	107	-054	161
58	1175	1171	4	1903	0526	1377	149	099	50
59	1175	1172	3	2244	0501	1743	129	135	6
60	1175	1176	1	2244	1278	966	129	081	48
61	1186	1184	2	2277	0899	1378	133	135	2
62	1196	1194	2	2310	2975	665	137	-042	179
63	1196	1196	0	2310	1806	504	137	079	58
64	1200	1200	0	2714	2163	551	093	100	7
65	1206	1212	6	1964	0279	1685	164	163	1
66	1211	1212	1	2610	1778	832	120	153	33
67	1288	1286	2	2605	0514	2091	183	173	10
68	1293	1291	2	2958	0118	2840	153	213	60
69	1293	1294	1	2958	2184	774	153	409	256
70	1313	1315	2	3047	3371	324	162	—	—
71	1340	1338	2	3440	1501	1939	142	169	27
72	1351	1348	3	2793	2609	184	220	106	114
73	1400	1405	5	3700	1713	1987	165	459	294
74	1420	1415	5	3885	3315	570	137	1138	1001
75	1570	1575	5	4816	2814	2002	191	157	34

# TABLE VII.

## 1. Wood Spirit ( $\epsilon = .001120$ ).

	$V_P$	$V_K$	$\Delta_{P-K}$	$\Delta^2$	$V_{P-K}$	$V_\epsilon$	$\Delta_{P,K-\epsilon}$	$\Delta^2$
10°	1.01203	1.01149	+ 54	2916	1.01176	1.01144	+32	1024
20°	1.02442	1.02330	+112	12544	1.02386	1.02339	+47	2209
30°	1.03724	1.03549	+175	30625	1.03636	1.03589	+47	2209
40°	1.05053	1.04810	+243	59049	1.04931	1.04901	+30	900
50°	1.06436	1.06120	+316	99856	1.06278	1.06280	- 2	4
60°	1.07875	1.07483	+392	153664	1.07679	1.07730	-51	2601
				358654				8947

## 2. Alcohol ( $\epsilon = .001020$ ).

	$V_P$	$V_K$	$\Delta_{P-K}$	$\Delta^2$	$V_{P,K}$	$V_\epsilon$	$\Delta_{P,K-\epsilon}$	$\Delta^2$
10°	1.01067	1.01051	+16	256	1.01059	1.01039	+20	400
20°	1.02169	1.02127	+42	1764	1.02148	1.02121	+27	729
30°	1.03309	1.03242	+67	4489	1.03275	1.03247	+28	784
40°	1.04486	1.04403	+83	6889	1.04444	1.04422	+22	484
50°	1.05701	1.05622	+79	6241	1.05661	1.05649	+12	144
60°	1.06953	1.06909	+44	1936	1.06931	1.06933	- 2	4
70°	1.08247	1.08276	-29	841	1.08261	1.08282	-21	441
				22416				2986

## 3. Ether ( $\epsilon = .001475$ ).

	$V_P$	$V_K$	$\Delta_{P-K}$	$\Delta^2$	$V_{P,K}$	$V_\epsilon$	$\Delta_{P,K-\epsilon}$	$\Delta^2$
10°	1.01541	1.01518	+23	529	1.01530	1.01519	+11	121
20°	1.03152	1.03122	+30	900	1.03137	1.03131	+ 6	36
30°	1.04859	1.04828	+31	961	1.04844	1.04852	- 8	64
				2390				221

## 4. Aldehyde ( $\epsilon = .001645$ ).

	$V_P$	$V_K$	$\Delta_{P-K}$	$\Delta^2$	$V_{P,K}$	$V_\epsilon$	$\Delta_{P,K-\epsilon}$	$\Delta^2$
10°	1.01745	1.01616	+129	16641	1.01680	1.01700	-20	400
20°	1.03699	1.03371	+328	107584	1.03535	1.03522	+13	169
				114225				569



**TABLE VII. (continued).**

**5. Acetate of Ethyl ( $\epsilon = .001251$ ).**

	$V_P$	$V_K$	$\Delta_{P-K}$	$\Delta^2$	$V_{P,K}$	$V_\epsilon$	$\Delta_{P,K-\epsilon}$	$\Delta^2$
10°	1.01289	1.01297	- 8	64	1.01293	1.01282	+11	121
20°	1.02646	1.02647	- 1	1	1.02646	1.02624	+22	484
30°	1.04080	1.04051	+ 29	841	1.04065	1.04048	+17	289
40°	1.05601	1.05524	+ 77	5929	1.05562	1.05546	+16	256
50°	1.07217	1.07067	+150	22500	1.07142	1.07133	+ 9	81
60°	1.08934	1.08688	+246	60516	1.08811	1.08818	- 7	49
70°	1.10770	1.10400	+370	136900	1.10580	1.10610	-30	900
				226751				2180

**6. Acetate of Methyl ( $\epsilon = .001285$ ).**

	$V_P$	$V_K$	$\Delta_{P-K}$	$\Delta^2$	$V_{P,K}$	$V_\epsilon$	$\Delta_{P,K-\epsilon}$	$\Delta^2$
10°	1.01325	1.01317	+ 8	64	1.01321	1.01317	+ 4	16
20°	1.02712	1.02717	- 5	25	1.02715	1.02705	+10	100
30°	1.04162	1.04198	- 36	1296	1.04180	1.04168	+12	144
40°	1.05677	1.05767	- 90	8100	1.05722	1.05715	+ 7	49
50°	1.07260	1.07423	-163	26569	1.07341	1.07358	-17	289
				36054				598

**7. Formate of Ethyl ( $\epsilon = .001294$ ).**

	$V_P$	$V_K$	$\Delta_{P-K}$	$\Delta^2$	$V_{P,K}$	$V_\epsilon$	$\Delta_{P,K-\epsilon}$	$\Delta^2$
10°	1.01355	1.01369	-14	196	1.01362	1.01327	+35	1225
20°	1.02770	1.02764	+ 6	36	1.02767	1.02725	+42	1764
30°	1.04251	1.04210	+41	1681	1.04235	1.04200	+35	1225
40°	1.05800	1.05728	+72	5184	1.05764	1.05760	+ 4	16
50°	1.07423	1.07345	+78	6084	1.07384	1.07419	-35	1225
				13181				5455

TABLE VII. (continued).

8. Fusel-oil ( $\epsilon = .00090$ ).

	$V_P$	$V_K$	$\Delta_{P-K}$	$\Delta^2$	$V_{P,K}$	$V_\epsilon$	$\Delta_{P,K-\epsilon}$	$\Delta^2$
$-10^\circ$	0.99115	0.99017	+ 98	9604	0.99066	0.99115	- 49	2401
$+10^\circ$	1.00898	1.00966	- 68	4624	1.00932	1.00915	+ 17	289
$20^\circ$	1.01816	1.01927	-111	12321	1.01871	1.01861	+ 10	100
$30^\circ$	1.02761	1.02894	-133	17689	1.02827	1.02842	- 15	225
$40^\circ$	1.03741	1.03881	-140	19600	1.03811	1.03859	- 48	2304
$50^\circ$	1.04762	1.04900	-138	19044	1.04831	1.04914	- 83	6889
$60^\circ$	1.05832	1.05960	-128	16384	1.05896	1.06011	-115	13225
$70^\circ$	1.06958	1.07079	-121	14641	1.07018	1.07152	-134	17956
$80^\circ$	1.08148	1.08263	-115	13225	1.08205	1.08342	-137	18769
$90^\circ$	1.09384	1.09522	-138	19044	1.09453	1.09581	-128	16384
$100^\circ$	1.10690	1.10890	-200	40000	1.10790	1.10880	- 90	8100
$110^\circ$	1.12060	1.12340	-280	78400	1.12200	1.12330	-130	16900
$120^\circ$	1.13520	1.13930	-410	168100	1.13720	1.13650	+ 70	4900
$130^\circ$	1.15070	1.15740	-670	448900	1.15400	1.15150	+250	62500
				881576				170942

9. Butyrate of Methyl ( $\epsilon = .00114$ ).

	$V_P$	$V_K$	$\Delta_{P-K}$	$\Delta^2$	$V_{P,K}$	$V_\epsilon$	$\Delta_{P,K-\epsilon}$	$\Delta^2$
$10^\circ$	1.01248	1.01215	+ 33	1089	1.01232	1.01165	+ 67	4489
$20^\circ$	1.02515	1.02472	+ 43	1849	1.02494	1.02383	+111	12321
$30^\circ$	1.03811	1.03778	+ 33	1089	1.03795	1.03659	+136	18496
$40^\circ$	1.05144	1.05137	+ 7	49	1.05141	1.04998	+143	20449
$50^\circ$	1.06519	1.06555	- 36	1296	1.06537	1.06408	+129	16641
$60^\circ$	1.07946	1.08039	- 93	8649	1.07993	1.07894	+ 99	9801
$70^\circ$	1.09435	1.09595	-160	25600	1.09515	1.09463	+ 52	2704
$80^\circ$	1.10990	1.11230	-240	57600	1.11110	1.11130	- 20	400
$90^\circ$	1.12620	1.12950	-330	108900	1.12780	1.12890	-110	12100
$100^\circ$	1.14340	1.14750	-410	168100	1.14540	1.14760	-220	48400
				374221				145801

TABLE VII. (concluded).

10. Butyrate of Ethyl ( $\epsilon = .001111$ ).

	$V_P$	$V_K$	$\Delta_{P-K}$	$\Delta^2$	$V_{P,K}$	$V_\epsilon$	$\Delta_{P,K-\epsilon}$	$\Delta^2$
10°	1.01206	1.01192	+ 14	196	1.01199	1.01135	+ 64	4096
20°	1.02427	1.02416	+ 11	121	1.02421	1.02319	+102	10404
30°	1.03676	1.03678	- 2	4	1.03677	1.03558	+119	14161
40°	1.04970	1.04983	- 13	169	1.04976	1.04857	+119	14161
50°	1.06317	1.06338	- 21	441	1.06327	1.06222	+105	11025
60°	1.07723	1.07745	- 12	144	1.07739	1.07656	+ 83	6889
70°	1.09233	1.09216	+ 17	289	1.09224	1.09169	+ 55	3025
80°	1.10830	1.10750	+ 80	6400	1.10790	1.10770	+ 20	400
90°	1.12540	1.12360	+180	32400	1.12450	1.12460	- 10	100
100°	1.14360	1.14050	+310	96000	1.14200	1.14250	- 50	2500
110°	1.16330	1.15810	+520	270400	1.16070	1.16170	-100	10000
				406564				76761

11. Butyric Acid ( $\epsilon = .000924$ ).

	$V_P$	$V_K$	$\Delta_{P-K}$	$\Delta^2$	$V_{P,K}$	$V_\epsilon$	$\Delta_{P,K-\epsilon}$	$\Delta^2$
10°	1.01035	1.01052	- 17	289	1.01043	1.00940	+103	10609
20°	1.02089	1.02118	- 29	841	1.02103	1.01913	+190	36100
30°	1.03162	1.03204	- 42	1764	1.03183	1.02923	+260	67600
40°	1.04261	1.04309	- 48	2304	1.04285	1.03971	+314	98596
50°	1.05383	1.05438	- 55	3025	1.05410	1.05060	+350	122500
60°	1.06533	1.06594	- 61	3721	1.06563	1.06194	+369	136161
70°	1.07713	1.07783	- 70	4900	1.07748	1.07377	+371	137641
80°	1.08923	1.09006	- 83	6889	1.08964	1.08611	+353	124609
90°	1.10170	1.10260	- 90	8100	1.10210	1.09905	+305	93025
100°	1.11450	1.11560	-110	12100	1.11500	1.11250	+250	62500
110°	1.12760	1.12910	-150	22500	1.12830	1.12740	+ 90	8100
120°	1.14120	1.14300	-180	32400	1.14210	1.14150	+ 60	3600
130°	1.15500	1.15740	-240	57600	1.15620	1.15710	- 90	8100
140°	1.16940	1.17230	-290	84100	1.17080	1.17350	-270	72900
150°	1.18410	1.18780	-370	136900	1.18590	1.19100	-510	260100
				377433				1242141

# VIII. Expansion of Liquids according to Thorpe. (D. Mendeleeff.)

	10°	30°	60°	100°	150°	
$\text{PCl}_6\text{H}_5\text{Cl}_2$ . . . . .	1.0083	1.0250	1.0507	1.0869	1.1368	From <i>Pinus sabiniana</i> , boiling at 98°.4, sp. gr. at o° = 0.70048.
$\text{PBr}_3$ . . . . .	1.0085	1.0259	1.0530	1.0916	1.1450	
$\text{NC}_6\text{H}_5\text{H}_2$ , aniline . . . . .	1.0087	1.0262	1.0535	1.0925	1.1473	
$\text{SO}_2(\text{OH})\text{Cl}$ . . . . .	1.0091	1.0273	1.0552	1.0941	1.1465	
$\text{C}_2\text{H}_5\text{Cl}$ . . . . .	1.0095	1.0285	1.0578	1.0994	1.1585	
$\text{S}_2\text{Cl}_2$ . . . . .	1.0094	1.0285	1.0584	1.1016	1.1618	
$\text{CHBr}_3$ . . . . .	1.0094	1.0287	1.0584	1.1012	—	
$\text{ICl}^*$ . . . . .	1.0093	1.0283	1.0586	1.1027	—	
$\text{C}_2\text{H}_4\text{ICl}$ . . . . .	1.0094	1.0286	1.0587	1.1023	—	
$(\text{CH}_2\text{Br})_2$ . . . . .	1.0096	1.0293	1.0605	1.1061	—	
$\text{S}_2\text{O}_5\text{Cl}_2$ . . . . .	1.0098	1.0299	1.0616	1.1074	—	¶ Ethyl-amyli, boiling at 90°.3, sp. gr. at o° = 0.69692.
$\text{CrO}_2\text{Cl}_2$ . . . . .	1.0097	1.0298	1.0618	1.1086	—	
$\text{VOCl}_3$ . . . . .	1.0097	1.0298	1.0618	1.1087	—	
$\text{TiCl}_4$ . . . . .	1.0099	1.0301	1.0619	1.1084	—	
$\text{NC}_6\text{H}_7$ , picoline . . . . .	1.0098	1.0299	1.0620	1.1097	—	
$\text{POBrCl}_2$ . . . . .	1.0101	1.0307	1.0630	1.1098	—	
$\text{AsCl}_3$ . . . . .	1.0100	1.0306	1.0631	1.1104	—	
$\text{PSCl}_3$ . . . . .	1.0102	1.0310	1.0639	1.1121	—	
$\text{C}_8\text{H}_5\text{OCl}$ , epichlorhydrin . . . . .	1.0103	1.0315	1.0653	1.1155	—	
$\text{C}_3\text{H}_5\text{OH}$ , allyl alcohol . . . . .	1.0103	1.0314	1.0660	1.1204	—	
$\text{P}(\text{C}_2\text{H}_5\text{O})\text{Cl}_2$ † . . . . .	1.0104	1.0324	1.0680	1.1204	—	† Octane from methyl-hexyl-carbinol, boiling at 125°.46, sp. gr. at o° = 0.71883.
$\text{C}_2\text{Cl}_3\text{OCl}$ . . . . .	1.0110	1.0332	1.0682	1.1201	—	
$\text{CBrCl}_3$ . . . . .	1.0109	1.0332	1.0686	1.1206	—	
$\text{POCl}_3$ . . . . .	1.0109	1.0333	1.0693	1.1232	—	
$\text{C}(\text{NO}_2)\text{Cl}_3$ . . . . .	1.0111	1.0337	1.0694	1.1226	—	
$\text{Br}_2$ . . . . .	1.0108	1.0335	1.0698	—	—	
$\text{C}_2\text{Cl}_3\text{OH}$ . . . . .	1.0111	1.0347	1.0719	—	—	
$\text{SnCl}_4$ . . . . .	1.0117	1.0356	1.0736	1.1302	—	
$\text{CH}_2\text{ClCH}_2\text{Cl}$ . . . . .	1.0116	1.0356	1.0742	—	—	
$\text{CS}_2$ . . . . .	1.0116	1.0360	—	—	—	
$\text{C}_8\text{H}_{18}$ ‡ . . . . .	1.0119	1.0360	1.0745	1.1331	—	* For a body like iodine monochloride, we can assume with De Heen, that it begins to dissociate on heating already when liquid, sooner than it distils. ‡ $\text{PCl}_3 + \text{C}_2\text{H}_5\text{OH} = \text{HCl} + \text{P}(\text{C}_2\text{H}_5\text{O})\text{Cl}_2$
$\text{SOCl}_2$ . . . . .	1.0117	1.0360	1.0752	—	—	
$\text{PCl}_3$ . . . . .	1.0117	1.0360	1.0755	—	—	
$\text{C}_8\text{H}_{18}$ § . . . . .	1.0120	1.0368	1.0771	1.1401	—	
$\text{CCl}_4$ . . . . .	1.0121	1.0372	1.0778	—	—	
$\text{C}_7\text{H}_{16}$    . . . . .	1.0122	1.0376	1.0792	1.1439	—	
$\text{SO}_2\text{Cl}_2$ . . . . .	1.0124	1.0380	1.0797	—	—	
$\text{C}_7\text{H}_{16}$ ¶ . . . . .	1.0125	1.0386	1.0815	—	—	
$\text{CHCl}_3$ . . . . .	1.0125	1.0387	1.0818	—	—	
$\text{NC}_3\text{H}_5$ , propionitril . . . . .	1.0125	1.0388	1.0820	1.1479	—	
$\text{CH}_3\text{CHCl}_2$ . . . . .	1.0130	1.0404	1.0855	—	—	
$\text{CH}_2\text{Cl}_2$ . . . . .	1.0134	1.0417	—	—	—	
$\text{SiCl}_4$ . . . . .	1.0136	1.0425	1.0904	—	—	
$\text{AsF}_3$ . . . . .	1.0144	1.0433	1.0885	—	—	
$\text{CO}(\text{CH}_3)_2$ , acetone . . . . .	1.0138	1.0433	1.0920	—	—	
$\text{C}_2\text{H}_3\text{OCl}$ . . . . .	1.0139	1.0433	—	—	—	
$(\text{NO}_2)_2$ . . . . .	1.0157	—	—	—	—	

# IX. Comparison of Mendelejeff's formula with the mean results of Kopp and Pierre.

t°	V <sub>P,K</sub>	V <sub>M</sub>	Δ	Δ <sup>2</sup>	t°	V <sub>P,K</sub>	V <sub>M</sub>	Δ	Δ <sup>2</sup>
(1) Wood Spirit.					(8) Fusel-oil.				
10	1.01176	1.01195	-19	361	-10	0.99066	0.99035	31	961
20	1.02386	1.02420	-34	1156	10	1.00932	1.00983	-51	2601
30	1.03636	1.03675	-39	1521	20	1.01871	1.01987	-126	15876
40	1.04931	1.04960	-29	841	30	1.02827	1.03010	-183	33489
50	1.06278	1.06278	0	0	40	1.03811	1.04054	-243	59049
60	1.07679	1.07629	50	2500	50	1.04831	1.05118	-287	82369
				6379	60	1.05896	1.06205	-309	95481
					70	1.07018	1.07315	-297	88209
					80	1.08205	1.08448	-243	59049
					90	1.09453	1.09606	-153	23409
					100	1.10790	1.10790	0	0
					110	1.12200	1.11998	202	40804
					120	1.13720	1.13234	486	236196
					130	1.15400	1.14496	904	817216
									1552709
(2) Alcohol.					(9) Butyrate of Methyl.				
10	1.01059	1.01092	-33	1089	10	1.01232	1.01266	-34	1156
20	1.02148	1.02208	-60	3600	20	1.02494	1.02564	-70	4900
30	1.03275	1.03349	-74	5476	30	1.03795	1.03896	-101	10201
40	1.04444	1.04516	-72	5184	40	1.05141	1.05263	-122	14884
50	1.05661	1.05710	-49	2401	50	1.06537	1.06667	-130	16900
60	1.06931	1.06931	0	0	60	1.07993	1.08107	-114	12996
70	1.08261	1.08181	80	6400	70	1.09515	1.09588	-73	5329
				24150	80	1.11110	1.11110	0	0
					90	1.12780	1.12675	105	11025
					100	1.14540	1.14284	256	65536
									142927
(3) Ether.					(10) Butyrate of Ethyl.				
10	1.01530	1.01564	-34	1156	10	1.01199	1.01246	-47	2209
20	1.03137	1.03178	-41	1681	20	1.02421	1.02522	-101	10201
30	1.04844	1.04844	0	0	30	1.03677	1.03832	-155	24025
				2837	40	1.04976	1.05175	-199	39601
					50	1.06327	1.06554	-227	51529
					60	1.07739	1.07969	-230	52900
					70	1.09224	1.09424	-200	40000
					80	1.10790	1.10916	-126	15876
					90	1.12450	1.12450	0	0
					100	1.14200	1.14027	173	29929
					110	1.16070	1.15650	420	176400
									442670
(4) Aldehyde.					(11) Butyric Acid.				
10	1.01680	1.01737	-57	3249	10	1.01043	1.01048	-5	25
20	1.03535	1.03535	0	0	20	1.02103	1.02118	-15	225
				3249	30	1.03183	1.03210	-27	729
					40	1.04285	1.04327	-42	1764
					50	1.05410	1.05468	-58	3364
					60	1.06563	1.06634	-71	5041
					70	1.07743	1.07826	-83	6889
					80	1.08964	1.09045	-81	6561
					90	1.10210	1.10292	-82	6724
					100	1.11500	1.11568	-68	4624
					110	1.12830	1.12873	-43	1849
					120	1.14210	1.14219	0	0
					130	1.15620	1.15579	41	1681
					140	1.17080	1.16980	100	10000
					150	1.18590	1.18417	173	29929
									78600
(5) Acetate of Ethyl.									
10	1.01293	1.01368	-75	5625					
20	1.02646	1.02742	-96	9216					
30	1.04065	1.04220	-155	24025					
40	1.05562	1.05706	-144	20736					
50	1.07142	1.07237	-95	9025					
60	1.08811	1.08811	0	0					
70	1.10580	1.10433	147	21609					
				90236					
(6) Acetate of Methyl.									
10	1.01321	1.01372	-51	2601					
20	1.02715	1.02781	-66	4356					
30	1.04180	1.04231	-51	2601					
40	1.05722	1.05722	0	0					
50	1.07341	1.07256	85	7225					
				16783					
(7) Formate of Ethyl.									
10	1.01362	1.01381	-19	361					
20	1.02767	1.02801	-34	1156					
30	1.04235	1.04262	-27	729					
40	1.05764	1.05764	0	0					
50	1.07384	1.07310	74	5476					
				7722					

# X. Principal Argument in terms of the Expansion for 0° Centigrade.

°	0	1	2	3	4	5	6	7	8	9
.0000	1.0000	.9991	.9982	.9973	.9964	.9955	.9947	.9938	.9930	.9921
.0001	.9912	.9904	.9895	.9887	.9879	.9871	.9862	.9854	.9846	.9838
.0002	.9830	.9822	.9815	.9807	.9799	.9791	.9783	.9776	.9768	.9761
.0003	.9754	.9747	.9740	.9733	.9725	.9718	.9711	.9703	.9696	.9682
.0004	.9682	.9675	.9669	.9662	.9655	.9648	.9641	.9634	.9627	.9621
.0005	.9615	.9609	.9602	.9596	.9589	.9583	.9577	.9571	.9564	.9558
.0006	.9552	.9546	.9540	.9534	.9528	.9522	.9516	.9510	.9504	.9498
.0007	.9492	.9486	.9481	.9475	.9469	.9464	.9458	.9452	.9446	.9441
.0008	.9436	.9430	.9425	.9420	.9415	.9409	.9404	.9398	.9393	.9388
.0009	.9383	.9378	.9373	.9368	.9363	.9358	.9353	.9348	.9343	.9338
.0010	.9333	.9328	.9323	.9318	.9314	.9309	.9304	.9299	.9294	.9290
.0011	.9285	.9281	.9276	.9271	.9267	.9262	.9258	.9253	.9249	.9244
.0012	.9240	.9235	.9231	.9227	.9222	.9218	.9214	.9210	.9205	.9201
.0013	.9197	.9193	.9189	.9185	.9180	.9176	.9172	.9168	.9164	.9160
.0014	.9156	.9152	.9148	.9144	.9140	.9136	.9133	.9129	.9125	.9121
.0015	.9117	.9113	.9109	.9106	.9102	.9098	.9094	.9091	.9087	.9084
.0016	.9080	.9076	.9072	.9069	.9065	.9062	.9059	.9055	.9051	.9048
.0017	.9044	.9041	.9037	.9034	.9030	.9027	.9024	.9020	.9017	.9014
.0018	.9010	.9007	.9004	.9001	.8997	.8994	.8991	.8988	.8984	.8981
.0019	.8978	.8975	.8972	.8968	.8965	.8962	.8959	.8956	.8953	.8950
.0020	.8947	.8944	.8941	.8938	.8935	.8932	.8929	.8927	.8924	.8921

## XI. Absolute Critical Temperature in terms of the Principal Argument.

	0	1	2	3	4	5	6	7	8	9
.90	444.7	447.7	450.8	453.9	457.1	460.4	463.8	467.2	470.7	474.4
.91	478.0	481.8	485.7	489.7	493.7	497.9	502.2	506.6	511.1	515.7
.92	520.5	525.3	530.3	535.5	540.8	546.2	551.8	557.5	563.5	569.5
.93	575.8	582.3	588.9	595.8	602.9	610.2	617.8	625.6	633.6	642.0
.94	650.6	659.5	668.7	678.3	688.2	698.5	709.2	720.3	731.8	743.8
.95	756.3	769.3	782.9	797.0	811.8	827.2	843.3	860.3	878.0	896.6
.96	916.1	936.7	958.3	981.2	1005.3	1030.8	1057.8	1084.0	1117.0	1149.5
.97	1184.1	1212.2	1260.9	1303.6	1349.5	1399.2	1453.0	1508.1	1575.4	1645.4
.98	1722.4	1807.5	1902.0	2007.8	2121.9	2261.7	2415.9	2593.8	2801.4	3046.9
.99	3341.4	3701.4	4151.5	4730.3	5502.0	6582.5	8203.4	10905.0	16308.4	32518.9

**XII.  $\text{mED}^{-1}$  in terms of the Principal Argument.**

	0	1	2	3	4	5	6	7	8	9
$10^{11} \times$	4.526	4.649	4.776	4.907	5.042	5.182	5.327	5.477	5.633	5.794
	5.960	6.133	6.313	6.499	6.691	6.891	7.099	7.315	7.540	7.772
	8.015	8.267	8.530	8.805	9.090	9.388	9.698	10.020	10.360	10.710
$10^{12} \times$	1.108	1.147	1.188	1.230	1.275	1.321	1.370	1.422	1.476	1.533
	1.593	1.656	1.722	1.792	1.867	1.946	2.028	2.116	2.210	2.309
	2.414	2.526	2.645	2.773	2.909	3.055	3.211	3.378	3.558	3.752
	3.960	4.186	4.430	4.695	4.982	5.296	5.638	6.013	6.424	6.876
	7.376	7.929	8.544	9.230	9.999	10.860	11.840	12.950	14.210	15.670
$10^{13} \times$	1.735	1.931	2.161	2.433	2.758	3.151	3.633	4.232	4.987	5.960
	7.242	8.978	11.410	14.960	20.450	29.570	46.390	82.810	148.600	751.300

# XIII. $\text{LmK}^{-1}$ in terms of the Principal Argument and the Temperature.

Containing three significant figures.

	.90	.91	.92	.93	.94	.95	.96	.97	.98	.99
-10°	5492	6079	6822	7779	9061	10860	13560	17960	27040	54120
0°	5392	5987	6736	7696	8987	10780	13480	17900	26980	54060
10°	5288	5893	6648	7611	8910	10700	13400	17840	26910	53390
20°	5180	5796	6558	7525	8830	10630	13330	17780	26840	53920
30°	5068	5696	6466	7437	8748	10550	13260	17720	26770	53850
40°	4952	5592	6370	7347	8663	10470	13190	17660	26710	53780
50°	4828	5484	6272	7256	8579	10390	13120	17600	26640	53700
60°	4700	5372	6172	7163	8493	10320	13040	17540	26570	53630
70°	4567	5256	6068	7079	8405	10240	12970	17480	26500	53560
80°	4432	5136	5961	6983	8316	10160	12890	17410	26430	53490
90°	4293	5012	5851	6885	8226	10070	12820	17340	26360	53420
100°	4152	4882	5739	6785	8134	9990	12740	17270	26290	53340
110°	4009	4750	5625	6683	8040	9910	12660	17200	26220	53270
120°	3864	4616	5508	6578	7945	9820	12580	17130	26150	53200
130°	3726	4480	5388	6470	7849	9740	12500	17060	26080	53130
140°	3566	4342	5264	6360	7752	9650	12420	16990	26010	53050
150°	3414	4202	5139	6247	7654	9550	12330	16910	25940	52980



XIV.  $(H - H')$   $\text{mK}^{-1}$  in terms of the Principal Argument and the Temperature.  
Containing three significant figures.

	.90	.91	.92	.93	.94	.95	.96	.97	.98	.99
$-10^\circ$	9.527	8.995	8.514	8.077	7.683	7.322	6.993	6.693	6.415	6.159
$0^\circ$	9.870	9.253	8.709	8.225	7.792	7.403	7.050	6.730	6.437	6.169
$10^\circ$	10.253	9.539	8.919	8.383	7.904	7.485	7.108	6.766	6.460	6.176
$20^\circ$	10.697	9.857	9.108	8.548	8.024	7.569	7.166	6.807	6.479	6.187
$30^\circ$	11.208	10.210	9.400	8.724	8.152	7.659	7.226	6.845	6.505	6.197
$40^\circ$	11.806	10.613	9.677	8.919	8.285	7.751	7.286	6.883	6.525	6.208
$50^\circ$	12.525	11.065	9.977	9.128	8.424	7.850	7.351	6.925	6.548	6.218
$60^\circ$	13.398	11.603	10.317	9.347	8.578	7.947	7.417	6.967	6.571	6.228
$70^\circ$	14.486	12.215	10.697	9.589	8.735	8.055	7.485	7.007	6.598	6.239
$80^\circ$	15.902	12.953	11.123	9.857	8.908	8.162	7.558	7.050	6.621	6.247
$90^\circ$	17.752	13.837	11.612	10.147	9.088	8.276	7.627	7.094	6.645	6.257
$100^\circ$	20.365	14.925	12.165	10.463	9.282	8.398	7.703	7.138	6.669	6.268
$110^\circ$	24.351	16.341	12.807	10.822	9.503	8.523	7.780	7.183	6.693	6.279
$120^\circ$	30.400	18.055	13.570	11.216	9.715	8.658	7.862	7.233	6.720	6.289
$130^\circ$	42.543	20.421	14.472	11.658	9.956	8.797	7.943	7.279	6.745	6.299
$140^\circ$	70.837	23.726	15.568	12.165	10.217	8.946	8.029	7.329	6.770	6.308
$150^\circ$	269.18?	28.692	16.920	12.730	10.508	9.105	8.121	7.380	6.798	6.321

**XV.  $\text{Sm}^2\text{D}^2$  in terms of the Principal Argument and Temperature.**  
Containing three significant figures.

	0°	10°	20°	30°	40°	50°	60°	70°
.90	300	295	289	282	276	269	262	255
.91	333	328	323	317	311	305	299	293
.92	375	370	365	360	355	349	344	338
.93	429	424	419	414	409	404	399	394
.94	500	496	491	487	482	478	473	468
.95	600	596	592	587	583	578	574	569
.96	750	746	742	738	734	730	726	722
.97	1000	996	992	988	985	981	977	974
.98	1500	1497	1495	1492	1489	1485	1481	1477
.99	3000	2997	2993	2990	2987	2983	2980	2977

	80°	90°	100°	110°	120°	130°	140°	150°
.90	247	239	231	222	215	206	198	190
.91	286	279	272	264	257	249	242	234
.92	332	326	319	313	307	300	293	286
.93	389	383	378	372	366	360	354	348
.94	463	458	453	447	442	437	432	426
.95	565	561	556	552	547	542	537	532
.96	717	713	709	705	700	696	692	687
.97	970	966	962	958	954	950	946	941
.98	1472	1468	1464	1461	1457	1454	1450	1446
.99	2973	2970	2967	2963	2960	2956	2953	2950

# XVI. Variation of the Principal Argument with the Temperature.

	.90	.91	.92	.93	.94	.95	.96	.97	.98	.99
-10°	.9054	.9146	.9239	.9333	.9427	.9522	.9617	.9712	.9808	.9904
0°	.9000	.9100	.9200	.9300	.9400	.9500	.9600	.9700	.9800	.9900
10°	.8944	.9052	.9160	.9266	.9373	.9478	.9583	.9688	.9792	.9897
20°	.8884	.9002	.9118	.9232	.9345	.9456	.9566	.9675	.9785	.9893
30°	.8821	.8950	.9075	.9197	.9316	.9433	.9549	.9663	.9776	.9889
40°	.8754	.8895	.9030	.9160	.9287	.9410	.9532	.9651	.9769	.9885
50°	.8682	.8838	.8984	.9122	.9257	.9386	.9514	.9638	.9761	.9881
60°	.8605	.8776	.8935	.9084	.9226	.9363	.9496	.9625	.9753	.9877
70°	.8522	.8712	.8884	.9044	.9195	.9338	.9478	.9613	.9744	.9873
80°	.8431	.8643	.8831	.9002	.9162	.9314	.9459	.9600	.9736	.9870
90°	.8334	.8570	.8775	.8959	.9129	.9289	.9441	.9587	.9728	.9866
100°	.8227	.8492	.8717	.8915	.9095	.9263	.9422	.9574	.9720	.9862
110°	.8108	.8406	.8656	.8868	.9058	.9237	.9403	.9561	.9712	.9858
120°	.7987	.8320	.8591	.8820	.9024	.9210	.9383	.9547	.9703	.9854
130°	.7848	.8225	.8523	.8770	.8987	.9183	.9364	.9534	.9695	.9850
140°	.7709	.8124	.8451	.8717	.8949	.9155	.9344	.9520	.9687	.9847
150°	.7555	.8016	.8375	.8663	.8909	.9126	.9323	.9506	.9678	.9842

XVII. Critical Temperatures, Theoretical, Empirical and Observed.\*  
(Data from Thorpe and Rücker.)

	$V_t$	$t^\circ$	$T_{i \text{ obs.}}$	$T_{i \text{ em.}}$	$\Delta$	$\Delta^2$	$T_{i \text{ th.}}$	$\Delta$	$\Delta^2$
Acetate of Ethyl	{ 1.1040 K 1.1175 E	70 77.1	512.8 S 529.5 P	509.3 504.4	- 3.5 -25.1	12.25 630.01	533.9 532.9	21.1 3.4	445.21 11.56
Acetate of Isobutyl	1.1574 E	116.3	568.8 P	565.5	- 3.3	10.89	587.6	18.8	353.44
Acetate of Methyl	{ 1.0733 K 1.0873 E	50 57.1	502.8 S 512.8 P	503.9 493.3	+ 1.1 -19.5	1.21 380.25	522.9 519.1	20.1 6.3	404.01 39.69
Acetate of Propyl	1.1444 E	100.8	555.4 P	537.3	-18.1	327.61	562.9	+7.5	56.25
Acetic Acid	—	118.5	594.5 P	—	—	—	—	—	—
Acetone	1.07517 T	50	505.8 S	494.9	-10.9	118.81	503.1	-2.7	7.29
Benzene	{ 1.1064 K 1.1064 K	80 80	564.7 R 553.6 S	553.8 553.8	-10.9 + 0.2	118.81 .04	566.5 566.5	+1.8 12.9	3.24 166.41
Bisulphide of Carbon	1.0489 T	40	544.8 S	566.9	+22.1	488.41	561.7	16.9	285.61
Bromide of Ethyl	1.0578 Pr	40.0	509.0 P	503.2	- 5.8	33.64	519.5	10.5	110.25
Butyrate of Ethyl	1.1692 E	119.9	577.3 P	552.2	-25.1	630.01	580.3	3.0	9.00
Butyrate of Propyl	1.1975 E	142.7	599.6 P	570.6	-29.0	841.00	600.1	0.5	.25
Chloride of Allyl	1.0675 Z	46.0	513.7 P	501.5	-12.2	148.84	520.5	6.8	46.24
Chloride of Ethyl	1.0160 Pr	10	455.6 S	455.2	- 0.4	.16	477.3	21.7	470.89

\* E, Elsässer; K, Kopp; O, Oudemans; P, Pawlewski; Pr, Pierre; R, Ramsay; S, Sajotschewsky; T, Thorpe; Z, Zander.

# XVII. Critical Temperatures (continued).

	$V_t$	$t^\circ$	$T_1$ OBS.	$T_1$ EM.	$\Delta$	$\Delta^2$	$T_1$ TH.	$\Delta$	$\Delta^2$
Chloride of Ethylene	1.1076 T	83.5	556.0 P	567.6	+11.6	134.56	577.1	21.1	445.21
Chloride of Ethylidene	1.0854 T	59.9	527.5 P	518.4	- 9.1	82.81	536.0	8.5	72.25
Chloroform	1.08179 T	60	533.0 S	534.6	+ 1.6	2.56	546.8	13.8	190.44
[Diethylamine]	1.0787 O	50	593.0 S	480.4	-112.6	12678.76	507.5	85.5	7310.25]
Diisobutyl	1.1553 T	108.5	543.8 P	541.4	- 2.4	5.76	575.2	31.4	985.96
Ether	{ 1.0483 K	30	463.0 S	463.3	+ 0.3	.09	489.3	26.3	691.69
	{ 1.0483 K	30	468.5 R	463.3	- 5.2	27.04	489.3	20.8	432.64
Formate of Ethyl	1.0735 K	50	503.0 S	502.9	- 0.1	.01	521.9	18.9	357.21
Formate of Isoamyl	1.1611 E	123.3	577.6 P	582.3	+ 4.7	22.09	600.8	23.8	566.44
Formate of Propyl	1.1180 E	81.0	540.4 P	521.5	-18.9	357.21	545.7	5.3	28.09
Propionate of Ethyl	1.1424 E	98.3	553.6 P	532.1	-21.5	462.25	558.7	5.1	26.01
Propionate of Isobutyl	1.1926 E	136.8	591.7 P	561.4	-30.3	918.09	592.4	0.7	.49
Propionate of Methyl	1.1197 E	79.9	535.7 P	511.5	-24.2	585.64	538.7	3.0	9.00
Propionate of Propyl	1.1683 E	122.2	577.8 P	562.0	-15.8	249.64	587.6	9.8	96.04
Propionic Acid	1.1781 Z	140.5	612.9 P	602.7	-10.2	104.04	617.8	4.9	24.01
Tetrachloride of Carbon	—	81.3	507.9 P	—	—	—	—	—	—
Toluene	—	109.2	593.8 P	—	—	—	—	—	—
Trichloride of Phosphorus	1.0983 T	75.9	558.5 P	561.9	+ 3.4	11.56	570.8	12.3	151.29
Total (30 observations)	—			6705.		6486.			
Probable Error				7.7 ?		10.0		9.9	

TABLE XVIII.

Name of Liquid.	Melting Point.	Boiling Point.	Density.	Symbol.	Principal Argument.			References.
					From $\epsilon$	From $T_1$	From L or E	
Acetate of Amyl .	.	138	0.884	$C_5H_{11}OC_2H_3O$	.932		.932	VI. 56
“ “ Ethyl .	.	74	0.909	$C_2H_5OC_2H_3O$	.922	.920	.935	VII. 5; V. 7; IX. 5; XVII.
“ “ Isobutyl .	.			$(CH_3)_2C_2H_3OC_2H_3O$	.932	.929	.932	XVII.
“ “ Methyl .	.	58	0.912	$CH_3OC_2H_3O$	.920	.917	.932	VII. 6; V. 6; IX. 6; XVII.
“ “ Propyl .	.			$C_3H_7OC_2H_3O$	.928	.927	.928	XVII.
Acetic Acid .	.	117	1.080	$HOOC_2H_3O$	.935	.933	.918	VI. 43; XVII.
“ “ (anhydrous)	.	138	1.097	$(C_2H_3O)_2O$	.933		.933	“ 41
Acetone .	.	56	0.814	$(CH_3)_2CO$	.919	.917	.930	“ 72; XVII. [init.; § 5
Alcohol .	.	78	0.812	$C_2H_5OH$	.932	.922	.930	VII. 2; V. 2; IX. 2; § 3
Aldehyde .	.	22	0.803	$CH_3CHO$	.906		*	VII. 4; V. 3; IX. 4
Amyl Mercaptan .	.	120	0.855	$C_5H_{11}SH$	.933		.933	VI. 38
Aniline .	.	186	1.036	$C_6H_5NH_2$	.945		.945	“ 8
Benzene .	.	81	0.899	$C_6H_6$	.928	.927	.931	“ 60; XVII.
Benzoate of Amyl .	.	261	1.004	$C_5H_{11}OC_7H_5O$	.946		.946	“ 9
“ “ Ethyl .	.	213	1.066	$C_2H_5OC_7H_5O$	.944		.944	“ 19
“ “ Methyl .	.	200	1.103	$CH_3OC_7H_5O$	.942		.942	“ 16
Benzoic Acid .	121	250	1.084	$HOOC_7H_5O$	.948		.948	“ 5
“ “ Alcohol .	.	207	1.063	$C_7H_7OH$	.950		.950	“ 4
Bromide of Amyl .	.	119	1.166	$C_5H_{11}Br$	.933		.933	“ 42
“ “ Antimony .	90	275	3.641	$SbBr_3$	.952		.952	“ 1
“ “ Ethyl .	.	41	1.473	$C_2H_5Br$	.920	.918	.920	“ 71; XVII.

TABLE XVIII. (continued).

Name of Liquid.	Melting Point.	Boiling Point.	Density.	Symbol.	Principal Argument.			References.
					From $\epsilon$	From $T_1$	From L or E	
Bromide of Ethylene	20 .	133	2.163	$C_2H_4Br_2$	.939		.939	VI. 32
" Methyl	.	13	1.664	$CH_3Br$	.915		.915	" 74
" Phosphorus.	.	175	2.925	$PBr_3$	.945		.945	" 13
" Silicon	.	153	2.813	$SiBr_4$	.940		.940	" 25
Bromine	.	63	3.187	$Br_2$	.932		.924	" 40; § 5, fin.
Butyl (?)	.	109	0.714	$C_8H_{18}$	.928		.928	" 65 [xvii.
Butyrate of Ethyl	.	117	0.903	$C_2H_5OC_4H_7O$	.928	.930	.930	VII. 10; V. 10; IX. 10;
" Methyl	.	101	0.975	$CH_3OC_4H_7O$	.927		.940	VII. 9; V. 9; IX. 9
" Propyl	.	.	.	$C_3H_7OC_4H_8O$	.934	.934	.935	xvii.
Butyric Acid	.	160	0.985	$HOC_4H_7O$	.937		.949	VII. 11; V. 8; IX. 11
Carbonate of Ethyl	.	126	1.000	$(C_2H_5)_2O_2CO$	.930		.930	VI. 58
Chloral	.	100	1.518	$CCl_3CHO$	.926		.926	" 26
Chloride of Acetyl	.	56	1.130	$C_2H_3OCl$	.920		.920	" 70
" Allyl	.	.	.	$C_3H_5Cl$	.920	.919	.920	xvii.
" Amyl	.	102	0.891	$C_5H_{11}Cl$	.929		.929	VI. 59
" Antimony	73	224	2.675	$SbCl_3$	.948		.948	" 6
" Arsenic	.	134	2.205	$AsCl_3$	.938		.942	" 31
" Benzoyl	.	198	1.232	$C_7H_5OCl$	.945		.945	" 14
" Bichlorethyl	.	75	1.346	$CH_3CCl_3$	.924		.924	" 57
" Bichlorethylene	.	138	1.612	$(CHCl_2)_2$	.938		.938	" 17
" Butyl	.	123	1.095	$C_4H_9Cl$	.934		.934	" 18

TABLE XVIII. (continued).

Name of Liquid.	Melting Point.	Boiling Point.	Density.	Symbol.	Principal Argument.			References.
					From $\epsilon$	From $T_1$	From Prob. value	
Chloride of Carbon [Bi-]	.	79	1.630	$\text{CCl}_4$	.925	.917	.928	VI. 61; xvii.
" Chloroethyl .	.	65	1.241	$\text{CH}_3\text{CHCl}_2$	.925		.925	" 68. See Chl. Ethyl-
" Chloroethylene	.	114	1.422	$\text{CH}_2\text{ClCHCl}_2$	.934		.934	" 35
" Ethyl .	.	11	0.921	$\text{C}_2\text{H}_5\text{Cl}$	.910	.904	.903	" 75; xvii.
" Ethylene .	.	85	1.280	$(\text{CH}_2\text{Cl})_2$	.930	.927	.930	" 50; xvii.
" Ethylidene .	.	59	1.198	$\text{CH}_3\text{CHCl}_2$	.923	.921	.923	xvii. See Chl. Chlor-
" Phosphorus	.	79	1.616	$\text{PCl}_3$	.929	.927	.924	xvii.
" Silicon	.	59	1.524	$\text{SiCl}_4$	.920		.920	VI. 69
" Sulphur	.	144	1.706	$\text{S}_2\text{Cl}_2$	.940		.940	" 28
" Tin [Bi-]	.	116	2.267	$\text{SnCl}_4$	.931		.936	" 53
" Titanium .	.	136	1.761	$\text{TiCl}_4$	.937		.937	" 24
" Trichlorethylene.	.	154	1.663	$\text{C}_2\text{HCl}_3$	.940		.940	" 23
Chloroform .	.	63	1.525	$\text{CHCl}_3$	.926	.923	.928	" 49; xvii.
Cinnamate of Ethyl .	.	267	1.066	$\text{C}_2\text{H}_5\text{OC}_9\text{H}_7\text{O}$	.948		.948	" 7
Cuminol .	.	237	0.983	$\text{C}_{10}\text{H}_{12}\text{O}$	.946		.946	" 11
Cyanide of Methyl	.	72	0.835	$\text{CH}_3\text{CN}$	.925		.925	" 66
" Phenyl	.	192	1.023	$\text{C}_6\text{H}_5\text{CN}$	.942		.942	" 20
Cymene .	.	178	0.878	$\text{C}_{10}\text{H}_{14}$	.941		.941	" 22
Diethylamine	.	57		$(\text{C}_2\text{H}_5)_2\text{HN}$	.917	.933	.925	xvii.
Diisobutyl .	.	109	0.711	$([\text{CH}_3]_2\text{C}_2\text{H}_3)_2$	.930	.925	*.929	"
Ether .	.	35	0.736	$(\text{C}_2\text{H}_5)_2\text{O}$	.913	.906	.920	[§ 3, init.; § 5. VII. 3; v. 4; IX. 3; xvii.;

\* Mean from the Latent Heat and the Elasticity.



TABLE XVIII. (continued).

Name of Liquid.	Melting Point.	Boiling Point.	Density.	Symbol.	Principal Argument.			References.
					From €	From T <sub>l</sub>	From Prob. L or E value	
Formate of Ethyl .	.	54	0.940	$C_2H_5OCHO$	.920	.916	.929	VII. 7; V. 5; IX. 7; XVII.
" " Isoamyl	.	.	.	$C_4H_9CH_2OCHO$	.934	.930	.933	XVII.
" " Methyl	.	33	0.998	$CH_3OCHO$	.917	.	.920	VI. 73
" " Propyl	.	.	.	$C_3H_7OCHO$	.925	.924	.925	XVII.
Formic Acid .	.	105	1.223	$HOCHO$	.937	.	.910	VI. 34
Fusel-oil .	.	132	0.826	$C_5H_{11}OH$	.938	.	.951	VII. 8; V. 11; IX. 8
Iodide of Amyl .	.	148	1.468	$C_5H_{11}I$	.937	.	.937	VI. 29
" " Ethyl .	.	70	1.975	$C_2H_5I$	.928	.	.926	" 55
" " Methyl .	.	44	2.199	$CH_3I$	.924	.	.910	" 64
Mustard Oil .	.	152	1.028	$C_3H_5SCN?$	.936	.	.936	" 45
Naphthalene .	.	217	0.977	$C_{10}H_8$	.944	.	.944	" 3
Nitrate of Ethyl .	.	87	1.132	$C_2H_5ONO_2$	.925	.	.925	" 52
Nitrobenzene .	.	221	1.200	$C_6H_5NO_2$	.947	.	.947	" 10
Oil of Bitter Almonds .	.	179	1.064	$C_6H_5CHO$	.944	.	.944	" 21
Oxalate of Ethyl .	.	186	1.102	$(C_2H_5)_2O_2C_2O_2$	.935	.	.952	" 46
" " Methyl .	50	161	1.157	$(CH_3)_2O_2C_2O_2$	.938	.	.938	" 47
Phenol .	.	189	1.081	$C_6H_5OH$	.948	.	.948	" 2
Propionate of Ethyl	.	98	0.923	$C_2H_5OC_3H_7O$	.925	.926	.926	" 67; XVII.
" " Isobutyl .	.	.	.	$(CH_3)_2C_2H_5OC_3H_7O$	.933	.932	.933	XVII.
" " Methyl .	.	.	.	$CH_3OC_3H_7O$	.924	.923	.924	"
" " Propyl .	.	.	.	$C_3H_7OC_3H_7O$	.932	.930	.932	"

TABLE XVIII. (concluded).

Name of Liquid.	Melting Point.	Boiling Point.	Density.	Symbol.	Principal Argument. From $\epsilon$	Principal Argument. From $T_1$	Principal Argument. From Prob. L or E value	References.
Propionic Acid . . .	.	142	1.016	$\text{HOC}_3\text{H}_5\text{O}$	.935	.935	.936	VI. 48; XVII.
Protochloride of Carbon . . .	.	124	1.649	$\text{C}_2\text{Cl}_4$	.935	.935	.935	" 30
Salicylate of Methyl . . .	.	224	1.197	$\text{CH}_3\text{OC}_7\text{H}_5\text{O}_2$	.946	.946	.946	" 12
Succinate of Ethyl . . .	.	218	1.072	$(\text{C}_2\text{H}_5)_2\text{C}_4\text{H}_4\text{O}_4$	.940	.940	.940	" 36
Sulphide of Carbon [Bi-] . . .	.	48	1.293	$\text{CS}_2$	.928	.925	*.920	" 54; XVII.; § 3, init.;
" Ethyl . . .	.	91	0.837	$(\text{C}_2\text{H}_5)_2\text{S}$	.926	.926	.926	" 63
" Methyl [Bi-] . . .	.	113	1.064	$(\text{CH}_3)_2\text{S}_2$	.934	.934	.934	" 37
Sulphite of Ethyl . . .	.	160	1.106	$(\text{C}_2\text{H}_5)_2\text{O}_2\text{SO}$	.938	.938	.938	" 33
Sulphocyanide of Methyl . . .	.	133	1.088	$\text{CH}_3\text{SCN}$	.935	.935	.935	" 27
Terebene . . .	.	162	0.872	$\text{C}_{10}\text{H}_{16}?$	.940	.940	.943	" 15
Toluene . . .	.	111	0.880	$\text{C}_6\text{H}_5\text{CH}_3$	.933	.933	*.935	XVII.
Turpentine . . .	.	160	0.890	$\text{C}_{10}\text{H}_{16}$	.942	.942	.942	§ 3, init.; § 5.
Valeraldehyde . . .	.	94	0.822	$(\text{CH}_3)_2\text{C}_2\text{H}_3\text{CHO}$	.925	.925	.925	VI. 62
Valerate of Amyl . . .	.	189	0.879	$\text{C}_5\text{H}_{11}\text{OC}_5\text{H}_9\text{O}$	.935	.935	.935	" 39
" Methyl . . .	.	116	0.902	$\text{CH}_3\text{OC}_5\text{H}_9\text{O}$	.934	.934	.934	" 51
Valeric Acid . . .	.	176	0.956	$\text{HOC}_5\text{H}_9\text{O}$	.938	.938	.947	" 44
Water . . .	0°	100	1.000	$\text{H}_2\text{O}$	.944	.944	.948	§ 3, init.; § 16, fin.
Wood Spirit . . .	.	66	0.817	$\text{CH}_3\text{OH}$	.928	.928	.935	VII. 1; V. I; IX. I

\* Mean from the Latent Heat and the Elasticity.